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<p>(54) Title: HAIR COLORING COMPOSITIONS</p> <p>(57) Abstract</p> <p>A hair coloring composition comprising: (a) an inorganic peroxygen oxidising agent; and (b) an oxidative hair coloring agent; wherein the pH of each of components (a) and (b) is in the range of from about pH 1 to about pH 4.5 and wherein the pH of the composition is in the range of from about pH 1 to about pH 4.5. The products can provide excellent hair coloring and in-use efficacy benefits including excellent initial color and good wash fastness in combination with reduced hair damage at low pH.</p>		

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Hair Coloring Compositions

Technical Field

This invention relates to hair coloring compositions and processes for coloring hair, and more especially to hair coloring compositions comprising an inorganic peroxygen oxidising agent in combination with an oxidative hair coloring agent at an acidic pH of between about 1 and about 4.5.

Background of the Invention

The desire to alter the color of human hair is not a facet of modern times. Since the days of the Roman Empire the color of human hair has been routinely altered to accommodate the changes of fashion and style. However the attainment of precise initial colors which are retained by the hair for a desirable period has remained a more elusive goal. The difficulties in the development of hair coloring compositions which can deliver precise long-lasting colors are in part due to the inherent structure of the hair itself and in part due to the necessary conditions of effective hair coloration processes.

In general, the condition and structure of human hair is not regular along the length of the hair shaft. Human hair is subject to various chemical and mechanical treatments such as combing, brushing, shampooing, heating, perming as well as exposure to the sun. As such, the hair at the ends of the hair shaft will generally exhibit greater signs of damage relative to the new growth close to the scalp. This damage can lead to inconsistent coloration when the hair is dyed due to irregular uptake of the hair coloring agents along the length of the hair shaft.

Once the hair has been colored there is a desire for the color to be resistant to fading, as occasioned by the actions of washing (also known as wash fastness), perspiration, hair spray and other exterior factors such as the action of the sun, and further that the color be retained in a consistent manner for a predictable period of time. Additionally damage to the hair that can lead to irregular dye uptake as discussed above, can lead to

increased fading of the damaged portions of the hair and consequently, irregular levels of color fade over time. An additional difficulty commonly associated with the dyeing of human hair is the need for dye systems which avoid any adverse effect on the hair and skin of the user, such as brittle hair, or, irritation of the skin, or, staining (coloring) of the skin.

Thus, it would be desirable to develop a hair coloring composition which exhibits reduced fade, provides improved resistance to wash out during a regular cleansing regimen, can deliver substantially consistent hair color results throughout the hair, which has reduced irritant effect on the skin, which has reduced staining on the skin, which has reduced adverse effects on the hair of the user and also to develop a convenient and easy-to-use method for the delivery of such a hair coloring composition to the hair.

Over the years significant effort has been directed towards the elimination of many of the problems associated with the dyeing of human hair. Various approaches to hair dyeing have been developed, these include, direct action dyes, natural dyes, metallic dyes and oxidative dyes.

To color human or animal hair using oxidative dye technology the hair is generally treated with a mixture of oxidative hair coloring agents and an oxidising agent. Hydrogen peroxide is the most commonly used oxidising agent. However, in addition to oxidising the oxidative coloring agents, hydrogen peroxide treatment of the hair can also solubilise and decolorise the colored melanin component in the hair which can lead to undesirable hair qualities, such as brittleness and hair damage. This is in part due to the conditions of conventional peroxide treatment, as part of the hair coloring process, when conducted at high pH ($> \text{pH } 9$), extended exposure (from 10 to 60 minutes) and a relatively high concentration of oxidising solution (between about 20% to about 40% volume of oxygen i.e. about 6 - 12% wt.) in order to deliver effective dye oxidation.

Oxidative hair coloring agents and peroxygen oxidising agents can be used to deliver a variety of hair colors to the hair. However substantial improvement is needed in the areas of color saturation, color development,

precise initial color consistency, improved wash fastness, improved hair condition and levels of hair damage.

Thus there is a need for oxidative hair coloring compositions which effectively dye the hair but avoid or reduce damage to the hair, which can color the hair effectively and avoid or reduce irritation and/or staining to the skin of the user.

Typically, hair coloring compositions containing oxidative hair coloring agents are formulated at high pH (from about pH 9 to about pH 12) and commonly contain, in addition to the oxidative hair coloring agents and an inorganic peroxygen oxidising agent, peroxide activating agents and a variety of additional cosmetic, coloring agent and peroxygen oxidising agent stabilising agents. It is also known that enhanced oxidative hair coloring agent oxidation can be achieved via the use of a hair swelling agent (HSA). Such HSA's enhance the oxidising and coloring process by swelling the hair fibres to aid both the diffusion of the peroxygen oxidising agent and the oxidative hair coloring agents into the hair and enabling faster, more thorough dye oxidation and hair coloring. A common HSA is an aqueous (alkaline) solution containing a source of ammonia, such as ammonium hydroxide. However ammonia can cause skin irritation and in addition has an undesirable odour and can cause lacrimatory effects.

Thus, it would be desirable to develop a hair coloring composition having desirable odour characteristics comprising oxidative hair coloring agents which delivers improved hair coloring benefits and/or delivers faster hair coloring without the need for an HSA.

It has now been found that the combination of inorganic peroxygen oxidising agents with one or more oxidative hair coloring agents at a pH below the internal pH of hair, between about pH 1 to about pH 4.5, and optionally, certain, additional oxidising agents, in hair coloring compositions can deliver excellent initial hair color in combination with improved color and wash fastness of the hair color over time, desirable color saturation and vividness attributes, reduced hair damage, reduced skin irritation, reduced skin staining and more efficient dyeing. Furthermore, it has been found that the efficiency of color development

(color change) from the inorganic peroxygen oxidising agents and particular oxidative hair coloring agents of the present invention is improved under the low pH conditions according to the present invention. In addition, it has been found that the hair coloring compositions according to the present invention can deliver these excellent hair coloring attributes results with minimal hair damage, at low pH (about 1 to about 4.5).

It is an object of the present invention to provide low pH hair coloring compositions which deliver the combination of improved hair coloring attributes, such as, longer lasting color (reduced fade), initial color generation, increased color uptake and color consistency across hair types. Hair types as defined herein means hair of varying age and condition i.e. virgin untreated, grey, permed, bleached etc.

It is an additional object of the present invention to provide low pH hair coloring compositions which have reduced levels of skin irritation and/or skin staining versus conventional high pH systems and which impart minimal damage to the hair fibres and reduced staining of skin in combination with an acceptable odor.

It is a still further object of the present invention to provide low pH hair coloring compositions which exhibit increased efficacy (improved color development). Color development as defined herein, means, the change in the hair color, expressed in terms of Delta E, as defined in the Experimental section herein after. It is a yet further object of the present invention to provide coloring compositions with reduced damage to the skin and/or hair which can deliver equivalent color development (versus conventional high pH systems) in combination with improved washfastness and color consistency while using less dye and/or less of the oxidising agent.

It has been found that the above objects can be met by the low pH hair coloring compositions according to the present invention.

In addition, conventional, high pH, hair coloring compositions typically comprise at least two separately packaged components, which are generally, oxidising agent (at low pH) and oxidative hair coloring agents

(at high pH). These separately packaged components are admixed at high pH just prior to application to the hair. Such an admixing step can be messy and inconvenient to the user. Typically, conventional coloring compositions, comprising oxidising agent and oxidative hair coloring agent, need to be used soon after admixing due to degradation of the resulting coloring composition. As such, excess admixed coloring composition is disposed of after application of the required amount to the hair. It has been found that the oxidant(s) and dyes of the present invention can be admixed in a singly packaged low pH mixture with improved stability versus conventional, high pH, oxidative dye systems. The singly packaged low pH coloring compositions of the present invention are suitable for use in a multi-application format (i.e. the consumer can use a single package for several color applications over a period of time). It has also been found that, at low pH, both the oxidising agent and oxidative hair coloring agents are stable over time, and can be stored as such.

Thus it is another object of the present invention to provide singly packaged hair coloring compositions which are fast acting, simple to use, and re-usable.

It is a further object of the present invention to provide hair coloring compositions comprising stable, separately packaged oxidant(s) and oxidative hair coloring agent(s) which remain stable at low pH both when stored individually or when mixed.

All percentages are by weight of the final compositions in the form intended to be used unless specified otherwise.

Summary of the Invention

The subject of the present invention is a hair coloring composition suitable for the treatment of human or animal hair.

According to one aspect of the present invention, there is provided a hair coloring composition comprising:

- (a) an inorganic peroxygen oxidising agent; and
- (b) an oxidative hair coloring agent;

wherein the pH of each of (a) and (b) is in the range of from about 1 to about 4.5 and wherein the combined mixture of (a) and (b) has a pH in the range of from about 1 to about 4.5.

It is to be understood that the percentage weights of the composition components herein are expressed in terms of the total composition, and includes the composition when in the form of intended use.

According to a further aspect of the present invention, there is provided:

A method for coloring hair wherein a hair coloring mixture is present in a single package and applied directly to the hair and wherein the hair coloring mixture comprises:

- (a) an inorganic peroxygen oxidising agent; and
- (b) an oxidative hair coloring agent;

wherein the pH of each of (a) and (b), is in the range of from about 1 to about 4.5 and wherein the combined mixture of (a) and (b), has a pH in the range of from about 1 to about 4.5.

According to a still further aspect of the present invention, there is provided:

A method for coloring hair wherein a hair coloring composition is present as separately packaged components (a) and (b) and wherein the hair coloring composition comprises:

- (a) an inorganic peroxygen oxidising agent wherein the pH of (a), is in the range of from about 1 to about 4.5; and;

- (b) an oxidative hair coloring agent wherein the pH of (b), is in the range of from about 1 to about 4.5;

wherein each of (a) and (b) are stable at pHs in the range of from about 1 to about 4.5 and wherein the combined mixture of (a) and (b) is stable over time and has a pH in the range of from about 1 to about 4.5.

Detailed Description of the Invention

As used herein the term 'hair' to be treated may be 'living' i.e. on a living body or may be 'non-living' i.e. in a wig, hairpiece or other aggregation of non-living fibres, such as those used in textiles and fabrics. Mammalian, preferably human hair is preferred. However wool, fur and other melanin containing fibres are suitable substrates for the compositions according to the present invention.

As used herein the term 'hair coloring composition' is used in the broad sense in that it is intended to encompass compositions containing the combinations herein of a low pH (from about 1 to about 4.5) mixture of inorganic peroxygen based dye oxidising agent and an oxidative coloring agent. Moreover, it is also intended to include complex compositions which contain other components which may or may not be active ingredients. Thus, the term 'hair coloring composition' is intended to apply to compositions which contain, in addition to a mixture of active oxidising agents and oxidative coloring agents, such things as, by way of example, oxidising aids, sequestrants, stabilisers, thickeners, buffers, carriers, surfactants, solvents, antioxidants, polymers, non-oxidative dyes and conditioners.

As discussed above, the hair coloring compositions according to the present invention comprise an inorganic peroxygen based oxidising agent (a), in combination with an oxidative hair coloring agent (b) wherein the pH of each of (a) and (b) is in the range of from about 1 to about 4.5 and wherein the pH of the combined mixture of (a) and (b) is in the range of from about 1 to about 4.5. Preferably, the pH of either (a) and/or (b) is in the range of from about 1.5 to about 4.5, more preferably from about 2 to

about 4.4, most preferably from about 3.6 to about 4.3 and especially from about 3.8 to about 4.2 and wherein the preferred pH of the combined mixture of (a) and (b) is in the range of from about 1.5 to about 4.5, more preferably from about 2 to about 4.4, most preferably from about 3.6 to about 4.3 and especially from about 3.8 to about 4.2. In addition to the inorganic peroxygen oxidising agent, the compositions may optionally comprise (among other ingredients) a preformed organic peroxyacid oxidising agent. Organic peroxyacid as used herein is intended to cover any organic peroxy acid material which can act either alone or in combination with a peroxygen oxidising agent to oxidise dye precursors.

The Dye Oxidisation and Hair Coloring Processes

It is understood by those familiar in the art that to successfully color human or animal hair with oxidative dyes it is generally necessary to treat the hair with a mixture of oxidising agent and oxidative hair coloring agent. As herein before discussed the most common oxidising agent is hydrogen peroxide.

Hydrogen peroxide has a pKa in the range of from about 11.2 to about 11.6, and, as such is generally used as a dye oxidising agent at pHs in the range of from about 9 to about 12. Surprisingly, it has now been found that improved color development is observed in combination with improved color washfastness, in the low pH oxidative systems according to the present invention, at pHs in the range of from about pH 1 to about pH 4.5, preferably from about pH 3.8 to about pH 4.3, more preferably from pH 3.8 to about pH 4.2.

Inorganic Oxidising Agents

The compositions of the invention comprise as an essential feature at least one inorganic oxidising agent (hereinafter called 'inorganic peroxygen oxidising agent'). The inorganic peroxygen oxidising agent should be safe and effective for use in the compositions herein. Preferably, the inorganic peroxygen oxidising agents suitable for use herein will be soluble in the compositions according to the present invention when in liquid form

and/or in the form intended to be used. Preferably, inorganic peroxygen oxidising agents suitable for use herein will be water-soluble. Water soluble oxidising agents as defined herein means agents which have a solubility to the extent of about 10g in 1000ml of deionised water at 25°C ("Chemistry" C. E. Mortimer. 5th Edn. p277).

The inorganic peroxygen oxidising agents useful herein are generally inorganic peroxygen materials capable of yielding peroxide in an aqueous solution. Inorganic peroxygen oxidising agents are well known in the art and include hydrogen peroxide, inorganic alkali metal peroxides such as sodium periodate, sodium perbromate and sodium peroxide, and inorganic perhydrate salt oxidising compounds, such as the alkali metal salts of perborates, percarbonates, perphosphates, persilicates, persulphates and the like. These inorganic perhydrate salts may be incorporated as monohydrates, tetrahydrates etc. Mixtures of two or more of such inorganic peroxygen oxidising agents can be used if desired. While alkali metal bromates and iodates are suitable for use herein the bromates are preferred. Highly preferred for use in the compositions according to the present invention is hydrogen peroxide.

It has been found that, under the low pH conditions according to the present invention, it is possible to deliver both improved initial color development, color consistency, washfastness and color intensity versus conventional, high pH, systems (using equivalent levels of peroxide and dyes) and also equivalent color development (detailed hereinafter in the Experimental Data section in terms of Delta E) versus conventional systems at high pH, while using substantially less of the inorganic peroxygen oxidising agent (up to 75% less) as well as delivering equivalent color development versus conventional, high pH, systems while using substantially less oxidative hair coloring agent (up to 50% less). Thus, the low pH hair coloring compositions according to the present invention can be formulated to reduce the level of damage to the hair and levels of skin irritation and staining. Furthermore, as the low pH hair coloring compositions according to the present invention can be formulated without ammonia there are no ammonia related odor or skin irritation negatives associated with these compositions.

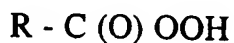
The inorganic peroxygen oxidising agent is present in the compositions according to the present invention at a molar level of from about 0.0003 moles (per 100g of composition) to less than about 0.09 moles (per 100g of composition), preferably, the inorganic peroxygen oxidising agent is present at a molar level of from about 0.0003 moles to about 0.08 moles, more preferably from about 0.0003 moles to about 0.06 moles, even more preferably from about 0.0003 moles to about 0.04 moles, most preferably from about 0.0003 mole to about 0.03 moles, especially from about 0.0003 moles to about 0.02 moles and most especially from about 0.0003 moles to about 0.015 moles (per 100g of composition).

In preferred compositions according to the present invention the inorganic peroxygen oxidising agent is present at a level of from about 0.01% to less than about 3%, preferably from about 0.01% to about 2.5%, more preferably from about 0.01% to about 2%, even more preferably from about 0.01% to about 1%, most preferably from about 0.01% to about 0.8%, especially from about 0.01% to about 0.55% and especially from about 0.01% to about 0.5% by weight of composition.

Preformed organic peroxyacid

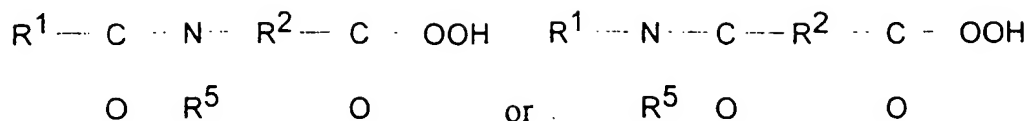
The compositions according to the present invention may, optionally, contain, in addition to the inorganic peroxygen oxidising agent(s), one or more preformed organic peroxyacid oxidising agents.

Suitable additional, optional, organic peroxyacid oxidising agents for use in the coloring compositions according to the present invention have the general formula:



wherein R is selected from saturated or unsaturated, substituted or unsubstituted, straight or branched chain, alkyl, aryl or alkaryl groups with from 1 to 14 carbon atoms.

A class of organic peroxyacid compounds suitable for use herein are the amide substituted compounds of the following general formulae:



wherein R^1 is, a saturated or unsaturated alkyl or alkaryl group, or an aryl group, having from 1 to 14 carbon atoms, R^2 is, a saturated or unsaturated alkyl or alkaryl group, or an aryl group, having from 1 to 14 carbon atoms, and R^5 is H or, a saturated or unsaturated alkyl or alkaryl group, or an aryl group, having from 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0,170,386.

Other suitable organic peroxyacid oxidising agents include peracetic, pernanoic, nonylamidoperoxyacaproic acid (NAPCA), perbenzoic, m-chloroperbenzoic, di-peroxy-isophthalic, mono-peroxyphthalic, peroxyauric, hexanesulphonyl peroxy propionic, N,N-phthaloylamino peroxyacaproic, monoper succinic, nonanoyloxybenzoic, dodecanedioyl-monoperoxybenzoic, nonylamide of peroxyadipic acid, diacyl and tetraacylperoxides, especially diperoxydodecanedioic acid, diperoxytetradecanedioic acid and diperoxyhexadecanedioic acid and derivatives thereof. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxyacaproic acid and derivatives thereof are also suitable for use herein.

The preformed organic peroxyacid oxidising agents should be safe and effective for use in the compositions herein. Preferably, the preformed organic peroxyacid oxidising agents suitable for use herein will be soluble in the compositions according to the present invention when in liquid form and in the form intended to be used. Preferably, preformed organic peroxyacid oxidising agents suitable for use herein will be water-soluble. Water soluble organic peroxyacid oxidising agents as defined herein means agents which have a solubility to the extent of about 10g in 1000ml of deionised water at 25°C ("Chemistry" C. E. Mortimer. 5th Edn. p277).

The preferred peroxyacid materials suitable for use herein are selected from peracetic and pernanoic acids and mixtures thereof.

The preformed organic peroxyacid oxidising agent, where present, is present at a molar level of from about 0.0001 moles to about 0.1 moles (per 100g of composition), more preferably from about 0.001 moles to about 0.05 moles, most preferably from about 0.003 moles to about 0.04 moles and especially from about 0.004 moles to about 0.03 moles per 100g of the hair coloring composition.

The preformed organic peroxyacid oxidising agent, where present, is preferably present at a level of from about 0.01% to about 8%, more preferably from about 0.1% to about 6%, most preferably from about 0.2% to about 4%, and especially from about 0.3% to about 3% by weight of the hair coloring composition. The weight ratio of the inorganic peroxygen oxidising agent to the preformed organic peroxy acid is preferably in the range of from about 0.0125:1 to about 500:1, more preferably from about 0.0125:1 to about 50:1.

In addition to the inorganic peroxygen oxidising agents and the additional, optional, preformed organic peroxyacid oxidising agents suitable for use herein, the compositions according to the present invention may optionally comprise additional organic peroxides such as urea peroxide, melamine peroxide and mixtures thereof. The level of organic peroxide, where present, is from about 0.01% to about 3%, preferably from about 0.01% to about 2%, more preferably from about 0.1% to about 1.5% and most preferably from about 0.2% to about 1% by weight of composition.

Hair Coloring Agents

The low pH hair coloring compositions of the present invention include as an essential feature an oxidative hair coloring agent. Such oxidative hair coloring agents are used in combination with the peroxide based oxidising systems of the present invention to formulate permanent, demi-permanent, semi-permanent or temporary hair dye compositions at low pH.

Permanent hair dye compositions as defined herein are compositions which once applied to the hair are substantially resistant to wash-out. Demi-permanent hair dye compositions as defined herein are

compositions which are substantially removed from the hair after up to 24 washes. Semi-permanent hair dye compositions as defined herein are compositions which once applied to the hair are substantially removed from the hair after up to 10 washes. Temporary hair dye compositions as defined herein are compositions which once applied to the hair are substantially removed from the hair after up to 2 washes. These different types of hair coloring compositions can be formulated via the specific combination of oxidant and/or dyes at different levels and ratios. Wash out as defined herein is the process by which hair color is removed from the hair over time during normal hair cleansing regimen. Washfastness as defined herein, means, the resistance of the dyed hair to wash out. Washfastness, as defined herein, can be measured in terms of the relative color change in the dyed hair (Delta E) over several washes (shampoos). Substantial removal of dye from the hair as defined herein means the color change in the dyed hair (Delta E) is greater than about 2 after up to 10 washes.

The concentration of each oxidative hair coloring agent in the low pH coloring compositions according to the present invention is from about 0.001% to about 3% by weight and is preferably from about 0.01% to about 2% by weight.

The total combined level of oxidative hair coloring agents in the compositions according to the present invention is from about 0.001% to about 5%, preferably from about 0.01% to about 4%, more preferably from about 0.1% to about 3%, most preferably from about 0.1% to about 1% by weight.

Typically, in conventional hair coloring compositions the total level of oxidative hair coloring agents present in the composition is in the range of from about 0.2% to about 3.5% by weight. Accordingly, the compositions according to the present invention can display improved hair coloring attributes, such as initial color development and initial color consistency in combination with improved washfastness over time, when compared to conventional, high pH, systems having similar levels of dye. Color consistency, as used herein, means, both the relative predictability

of the initial color development and improved color retention over time across different hair types.

The efficacy of the oxidative dyes is improved at low pH such that the compositions of the present invention are valuable for the delivery of good high intensity colors (dark colors) with reduced levels of dye. In particular, good hair coloring results in combination with equivalent color development (versus high pH systems) can be achieved using the inorganic peroxygen oxidising agents of the present invention and substantially less dye versus conventional, high pH, hair coloring compositions.

Thus according to a further aspect of the present invention there is provided a hair coloring composition comprising:

- (a) an inorganic peroxygen oxidising agent; and
- (b) an oxidative hair coloring agent;
- (c) a diluent suitable for application to the hair;

wherein the pH of each of (a) and (b) is in the range of from about 1 to about 4.5 and wherein the pH of the composition is in the range of from about 1 to about 4.5 .

As herein before described, it has also been found that the combination of inorganic peroxygen oxidising agents with oxidative hair coloring agent at low pH is valuable for the delivery of excellent hair coloring attributes in combination with reduced levels of hair damage, skin irritation and skin staining in combination with an improved odor profile (versus conventional high pH compositions). A further benefit of the low pH coloring compositions according to the present invention is that reduced levels of skin staining can be observed from such compositions, versus conventional, high pH, compositions.

Thus according to a still further aspect of the present invention there is provided a hair coloring composition capable of delivering a light auburn colour to light brown hair having 40% grey comprising:

- (a) an inorganic peroxygen oxidising agent;
- (b) an oxidative hair coloring agent; and
- (c) a diluent suitable for application to the hair;

wherein the pH of components (a) and (b) are each in the range of from about 1 to about 4.5 and wherein the pH of the composition is in the range of from about 1 to about 4.5 and wherein the change in level of skin staining after product application (Delta E) is less than about 4, preferably less than about 3, more preferably less than about 2.7. Light brown hair having 40% grey coverage is defined in terms of L, a, b values as having an 'L' value in the range of from about 35 to about 37, an 'a' value in the range of from about 4.5 to about 5.5 and a 'b' value in the range of from about 11.5 to about 12.7.

Without being limited by any particular theory, it is believed that, these improvements (in respect of reduced skin irritation and/ or staining) result from the combination of (a) reduced levels of dyes and low pH systems; (b) the reduction of paraphenylene diamine (PPD) contact sensitisation at low pH (high levels of PPD have been shown to display contact sensitisation at high pH, but not at low pH); (c) the elimination of the formation of nitrobenzene contact sensitisers (which can occur in high pH compositions); (d) reduced levels of skin staining at low pH versus high pH, and; (e) the reduction in skin irritation and odor negatives as a result of the elimination of ammonia and the use of alternative oxidising agents in the low pH dyeing compositions according to the present invention.

Oxidative Hair Coloring Processes

Any oxidative hair coloring agent can be used in the compositions according to the present invention. Typically, but without intending to be limited thereto, oxidative hair coloring agents, consist essentially of at least two components, which are collectively referred to as dye forming

intermediates (or precursors). Dye forming intermediates can react in the presence of a suitable oxidant to form a colored molecule.

The dye forming intermediates used in oxidative hair colorants include: aromatic diamines, aminophenols, various heterocycles, phenols, naphthols and their various derivatives. These dye forming intermediates can be broadly classified as; primary intermediates and secondary intermediates. Primary intermediates, which are also known as oxidative dye precursors, are chemical compounds which become activated upon oxidation and can then react with each other and/or with couplers to form colored dye complexes. The secondary intermediates, also known as color modifiers or couplers, are generally colorless molecules which can form colors in the presence of activated precursors/primary intermediates, and are used with other intermediates to generate specific color effects or to stabilise the color.

Primary intermediates suitable for use in the compositions and processes herein include: aromatic diamines, polyhydric phenols, amino phenols and derivatives of these aromatic compounds (e.g., N-substituted derivatives of the amines, and ethers of the phenols). Such primary intermediates are generally colorless molecules prior to oxidation.

While not wishing to be bound by any particular theory it is proposed herein that the process by which color is generated from these primary intermediates and secondary coupler compounds generally includes a stepwise sequence whereby the primary intermediate can become activated (by oxidation), and then enjoins with a coupler to give a dimeric, conjugated colored species, which in turn can enjoin with another 'activated' primary intermediate to produce a trimeric conjugated colored molecule.

Chemistry of Oxidative Hair Coloration Across pH

While not wishing to be bound by any particular theory, it is generally understood that conventional oxidative dyeing typically occurs between oxidative precursor molecules, oxidative coupler molecules and a

peroxygen oxidising agent at high pH (8 - 10). Typical precursors include 1,4-disubstituted benzene derivatives and typical couplers include 1,2- or 1,3-disubstituted benzene derivatives.

It is generally accepted that the pH within the hair shaft, of human hair, is around pH 5.5 to pH 6 (C.R. Robbins, Chemical and Physical Behaviour of Human Hair, 2nd Ed. p157) and that the hair has an inherent buffering capacity.

Surprisingly it has now been found that, oxidative hair coloration at pH 1 to 4.5 with oxidising agents and oxidative hair coloring agent is valuable for the delivery of excellent initial hair color in combination with improved color and wash fastness of the hair color over time, desirable color saturation and vividness attributes, reduced hair damage, reduced skin irritation, reduced skin staining and more efficient dyeing. Furthermore, it has been found that the efficiency of color development (i.e., increased color change) from the inorganic peroxygen oxidising agents and the oxidative hair coloring agents of the present invention is improved under the low pH conditions according to the present invention. In addition, it has been found that the low pH hair coloring compositions according to the present invention can deliver these excellent hair coloring attributes results with minimal hair damage.

It has also been found that at pH levels of from about 1.5 to about 4.5, preferably from about 2 to about 4.4, more preferably from about 3.6 to about 4.3, most preferably from about 3.8 to about 4.2 further improvements in color development can be achieved.

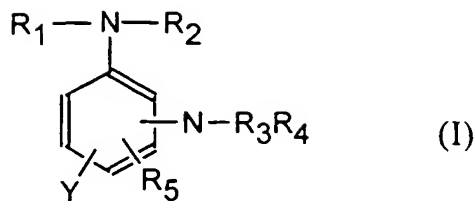
Oxidative Dye Precursors

In general terms, oxidative dye primary intermediates include those monomeric materials which, on oxidation, form oligomers or polymers having extended conjugated systems of electrons in their molecular structure. Because of the new electronic structure, the resultant oligomers and polymers exhibit a shift in their electronic spectra to the visible range and appear colored. For example, oxidative primary intermediates capable of forming colored polymers include materials such as aniline, which has a

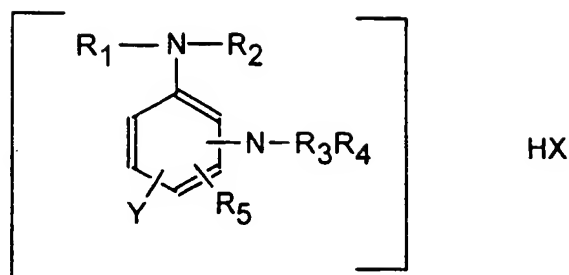
single functional group and which, on oxidation, forms a series of conjugated imines and quinoid dimers, trimers, etc. ranging in color from green to black. Compounds such as p-phenylenediamine, which has two functional groups, are capable of oxidative polymerization to yield higher molecular weight colored materials having extended conjugated electron systems. Oxidative dyes known in the art can be used in the low pH compositions according to the present invention. A representative list of primary intermediates and secondary couplers suitable for use herein is found in Sagarin, "Cosmetic Science and Technology," Interscience, Special Ed. Vol. 2 pages 308 to 310. It is to be understood that the primary intermediates detailed below are only by way of example and are not intended to limit the compositions and processes herein.

The typical aromatic diamines, polyhydric phenols, amino phenols, and derivatives thereof, described above as primary intermediates can also have additional substituents on the aromatic ring, e.g. halogen, aldehyde, carboxylic acid, nitro, sulfonic acid and substituted and unsubstituted hydrocarbon groups, as well as additional substituents on the amino nitrogen and on the phenolic oxygen, e.g. substituted and unsubstituted alkyl and aryl groups.

Examples of suitable aromatic diamines, amino phenols, polyhydric phenols and derivatives thereof, respectively, are compounds having the general formulas (I), (II) and (III) below:



OR



wherein Y is hydrogen, halogen, (e.g. fluorine, chlorine, bromine or iodine), nitro, amino, hydroxyl,



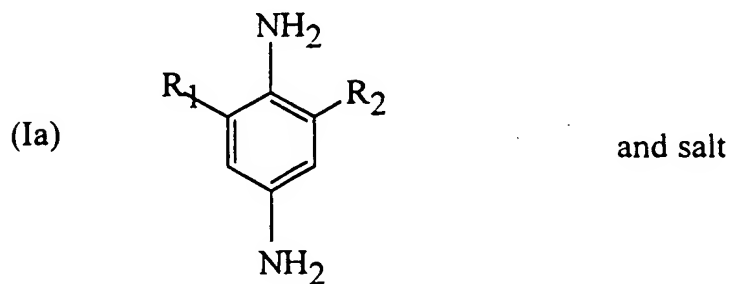
-COOM or -SO₃M. (where M is hydrogen or an alkali or alkaline earth metal, ammonium, or substituted ammonium wherein one or more hydrogens on the ammonium ion is replaced with a 1 to 3 carbon atom alkyl or hydroxyalkyl radical), wherein R₁, R₂, R₃ and R₄ are the same or different from each other and are selected from the group consisting of hydrogen, C₁ to C₄ alkyl or alkenyl and C₆ to C₉ aryl, alkaryl or aralkyl, and R₅ is hydrogen, C₁ to C₄ unsubstituted or substituted alkyl or alkenyl wherein the substituents are selected from those designated as Y, above, or C₆ to C₉ unsubstituted or substituted aryl, alkaryl or aralkyl wherein the substituents are selected from those defined as Y, above. Since the precursors of formula (I) are amines, they can be used herein in the form of

peroxide-compatible salts, as noted, wherein X represents peroxide-compatible anions of the type herein before detailed. The general formula of the salt indicated is to be understood to encompass those salts having mono-, di-, and tri-negative anions.

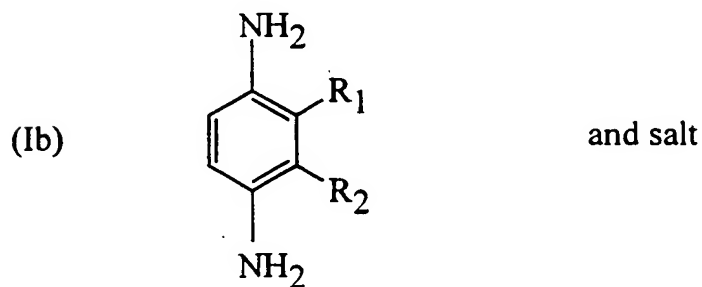
Specific examples of formula (I) compounds are: o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 2-chloro-p-phenylenediamine, 2-iodo-p-phenylenediamine, 4-nitro-o-phenylenediamine, 2-nitro-p-phenylenediamine, 1,3,5-triaminobenzene, 2-hydroxy-p-phenylenediamine, 2,4-diaminobenzoic acid, sodium 2,4-diaminobenzoate, calcium di-2,4-diaminobenzoate, ammonium 2,4-diaminobenzoate, trimethylammonium 2,4-, diaminobenzoate, tri-(2-hydroxyethyl)ammonium 2,4-diaminobenzoate, 2,4-diaminobenzaldehyde carbonate, 2,4-diaminobenzenesulfonic acid, potassium 2,4-diaminobenzenesulfonate, N,N-diisopropyl-p-, phenylenediamine bicarbonate, N,N-dimethyl-p-phenylenediamine, N-ethyl-N'-(2-propenyl)-p-phenylenediamine, N-phenyl-p-phenylenediamine, N-phenyl-N-benzyl-p-phenylenediamine, N-ethyl-N'-(3-ethylphenyl)-p-phenylenediamine, 2,4-toluenediamine, 2-ethyl-p-phenylenediamine, 2-(2-bromoethyl)-p-phenylenediamine, 2-phenyl-p-phenylenediamine laurate, 4-(2,5-diaminophenyl)benzaldehyde, 2-benzyl-p-phenylenediamine acetate, 2-(4-nitrobenzyl)-p-phenylenediamine, 2-(4-methylphenyl)-p-phenylenediamine, 2-(2,5-diaminophenyl)-5-methylbenzoic acid, methoxyparaphenylenediamine, dimethyl-p-phenylenediamine, 2,5-dimethylpara-phenylenediamine, 2-methyl-5-methoxy-para-phenylenediamine, 2,6-methyl-5-methoxy-para-phenylenediamine, 3-methyl-4-amino-N,N-diethylaniline, N,N-bis(β -hydroxyethyl)-para-phenylenediamine, 3-methyl-4-amino-N,N-bis(β -hydroxyethyl)aniline, 3-chloro-4-amino-N,N-bis(β -hydroxyethyl)aniline, 4-amino-N-ethyl-N-(carbamethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(carbamethyl)aniline, 4-amino-N-ethyl-(β -piperidonoethyl)aniline, 3-methyl-4-amino-N-ethyl-(β -piperidonoethyl)aniline, 4-amino-N-ethyl-N-(β -morpholinoethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(β -morpholinoethyl)aniline, 4-amino-N-ethyl-N-(β -acetylaminoethyl)aniline, 4-amino-N-(β -methoxyethyl) aniline, 3-methyl-4-amino-N-ethyl-N-(β -acetylaminoethyl) aniline, 4-amino-N-ethyl-N-(β -mesylaminoethyl) aniline, 3-methyl-4-amino-N-ethyl-N-(β -mesylaminoethyl) aniline, 4-amino-N-ethyl-N-(β -sulphoethyl) aniline, 3-

methyl-4-amino-N-ethyl-N-(β -sulphoethyl) aniline, N-(4-aminophenyl)morpholine, N-(4-aminophenyl)piperidine, 2,3-dimethyl-p-phenylenediamine, isopropyl-p-phenylenediamine, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine sulphate.

In highly preferred compositions according to the present invention the materials having general formulae (Ia) and (Ib) are preferred.



except where $R_1 = R_2 = \text{Me, Et}$

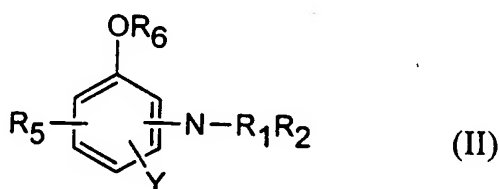


except where $R_1 = R_2 = \text{Me}$

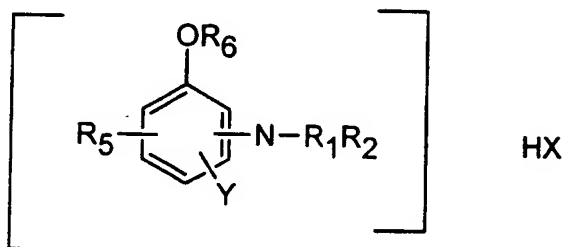
wherein Y is hydrogen, halogen, (e.g. fluorine, chlorine, bromine or iodine), nitro, amino, hydroxyl,



-COOM or -SO₃M (where M is hydrogen or an alkali or alkaline earth metal, ammonium, or substituted ammonium wherein one or more hydrogens on the ammonium ion is replaced with a 1 to 3 carbon atom alkyl or hydroxyalkyl radical), wherein R₁, R₂, R₃ and R₄ are the same or different from each other and are selected from the group consisting of hydrogen, C₁ to C₄ alkyl or alkenyl and C₆ to C₉ aryl, alkaryl or aralkyl, and R₅ is hydrogen, C₁ to C₄ unsubstituted or substituted alkyl or alkenyl wherein the substituents are selected from those designated as Y, above, or C₆ to C₉ unsubstituted or substituted aryl, alkaryl or aralkyl wherein the substituents are selected from those defined as Y, above. Since the precursors of formula (I) are amines, they can be used herein in the form of peroxide-compatible salts, as noted, wherein X represents peroxide-compatible anions of the type herein before detailed. The general formula of the salt indicated is to be understood to encompass those salts having mono-, di-, and tri-negative anions.



OR



where X and Y are the same as in formula (I), R₁ and R₂ can be the same or different from each other and are the same as in formula (I), R₅ is the

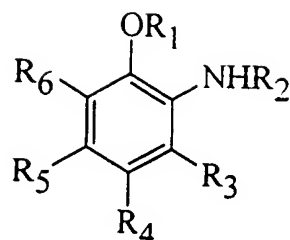
same as in formula (I) and R₆ is hydrogen or C₁ to C₄ substituted or unsubstituted alkyl or alkenyl wherein the substituents are selected from those defined as Y in formula (I).

Specific examples of formula (II) compounds are:

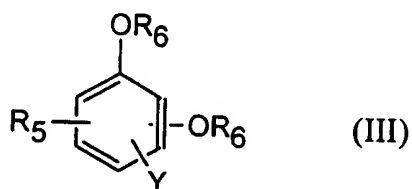
o-aminophenol, m-aminophenol, p-aminophenol, 2-iodo-p-aminophenol, 2-nitro-p-aminophenol, 3,4-dihydroxyaniline, 3,4-diaminophenol, chloroacetate, 2-hydroxy-4-aminobenzoic acid, 2-hydroxy-4-aminobenzaldehyde, 3-amino-4-hydroxybenzenesulfonic acid, N,N-diisopropyl-p-aminophenol, N-methyl-N-(1-propenyl)-p-aminophenol, N-phenyl-N-benzyl-p-aminophenol sulphate, N-methyl-N-(3-ethylphenyl)-p-aminophenol, 2-nitro-5-ethyl-p-aminophenol, 2-nitro-5-(2-bromoethyl)-p-aminophenol, (2-hydroxy-5-aminophenyl)acetaldehyde, 2-methyl-p-aminophenol, (2-hydroxy-5-aminophenyl)acetic acid, 3-(2-hydroxy-5-aminophenyl)-1-propene, 3-(2-hydroxy-5-aminophenyl)-2-chloro-1-propene, 2-phenyl-p-aminophenol palmitate, 2-(4-nitrophenyl)-p-aminophenol, 2-benzyl-p-aminophenol, 2-(4-chlorobenzyl-p-aminophenol perchlorate, 2-(4-methylphenyl)-p-aminophenol, 2-(2-amino-4-methylphenyl)-p-aminophenol, p-methoxyaniline, 2-bromoethyl-4-aminophenyl ether phosphate, 2-nitroethyl-4-aminophenyl ether bromide, 2-aminoethyl-4-aminophenyl ether, 2-hydroxyethyl-4-aminophenyl ether, (4-aminophenoxy)acetaldehyde, (4-aminophenoxy)acetic acid, (4-aminophenoxy)methanesulfonic acid, 1-propenyl-4-aminophenyl ether isobutyrate, (2-chloro)-1-propenyl-4-aminophenyl ether, (2-nitro)-1-propenyl-4-aminophenyl ether, (2-amino)-propenyl-4-aminophenyl ether, (2-hydroxy)-1-propenyl-4-aminophenyl ether, N-methyl-p-aminophenol, 3-methyl-4-aminophenol, 2-chloro-4-aminophenol, 3-chloro-4-aminophenol, 2,6-dimethyl-4-aminophenol, 3,5-dimethyl-4-aminophenol, 2,3-dimethyl-4-aminophenol, 2,5-dimethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 3-hydroxymethyl-4-aminophenol.

According to the present invention compounds having the following general formula are not preferred:

24



wherein: R_1 is alkyl, hydroxy alkyl, carboxyalkyl or aminoalkyl; R_2 is hydrogen, alkyl or hydroxyalkyl groups; R_3 and R_5 are H or -OR where R is an alkyl or hydroxyalkyl substituents; R_4 is H, alkyl or NHR' ; R_6 is H, alkyl, -OR or NHR' ; R' is H, alkyl, hydroxyalkyl : with the proviso that a) only one of R_4 and R_6 are NHR' ; b) R_3 and -OR₁ are not both methoxy when R_2 , R_5 and R_6 are H and R_4 is NH_2 ; c) either R_3 , or R_4 , or R_5 , or R_6 is H; d) R_3 , R_4 and R_5 are not all H when R_6 is NH_2 , R_2 is H and R_1 is methyl; e) if R_1 is ethyl and R_2 , R_3 , R_4 and R_6 are H, R_4 is not NH_2 ; f) if R_1 is carboxyalkyl or aminoalkyl, R_4 is NHR' .



(III)

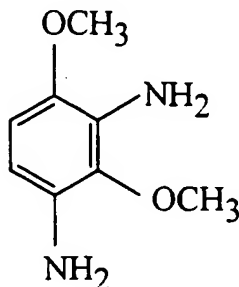
where Y, R_5 and R_6 are as defined above in formula (II).

Specific examples of formula (III) compounds are:

o-hydroxyphenol (catechol), m-hydroxyphenol (resorcinol), p-hydroxyphenol (hydroquinone), 4-methoxyphenol, 2-methoxyphenol, 4-(2-chloroethoxy) phenol, 4-(2-propenoxy) phenol, 4-(3-chloro-2-propenoxy) phenol, 2-chloro-4-hydroxyphenol (2-chlorohydroquinone), 2-nitro-4-hydroxyphenol(2-nitrohydroquinone), 2-amino-4-hydroxyphenol, 1,2,3-trihydroxybenzene (pyrogallol), 2,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzoic acid, 2,4-dihydroxybenzenesulfonic acid, 3-ethyl-4-hydroxyphenol, 3-(2-nitroethyl)-4-hydroxyphenol, 3-(2-propenyl)-4-hydroxyphenol, 3-(3-chloro-2-propenyl)-4-hydroxyphenol, 2-phenyl-4-hydroxyphenol, 2-(4-chlorophenyl)-4-hydroxyphenol, 2-benzyl-4-hydroxyphenol, 2-(2-nitrophenyl)-4-hydroxyphenol, 2-(2-methylphenyl)-4-hydroxyphenol, 2-(2-methyl-4-chlorophenyl)-4-hydroxyphenol, 3-

methoxy-4-hydroxy-benzaldehyde, 2-methoxy-4-(1-propenyl)phenol, 4-hydroxy-3-methoxycinnamic acid, 2,5-dimethoxyaniline, 2-methylresorcinol, alpha naphthol and salts thereof.

In preferred compositions herein the following compound, having the following formula is not included:



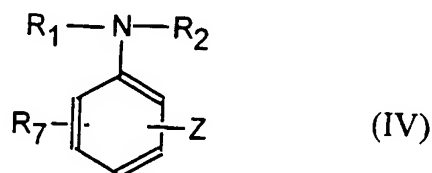
Secondary coupling compounds (color modifiers), such as those detailed hereinafter, are preferably used in conjunction with the primary intermediates herein and are thought to interpose themselves in the colored polymers during their formation and to cause shifts in the electronic spectra thereof, thereby resulting in slight color changes.

Secondary coupling compounds which are suitable for inclusion in the coloring compositions and processes herein before described include certain aromatic amines and phenols and derivatives thereof which do not produce color singly, but which modify the color, shade or intensity of the colors developed by the primary oxidized dye intermediates. Certain aromatic amines and phenolic compounds, and derivatives thereof, including some aromatic diamines and polyhydric phenols of the types described by formulas (I), (Ia), (Ib), (II) and (III) above, but which are well known in the art not to be suitable primary intermediates, are suitable as couplers herein. Polyhydric alcohols are also suitable for use as couplers herein.

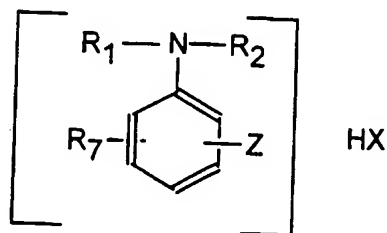
The aromatic amines and phenols and derivatives described above as couplers can also have additional substituents on the aromatic ring, e.g., halogen, aldehyde, carboxylic acid, nitro, sulfonyl and substituted and unsubstituted by hydrocarbon groups, as well as additional substituents on

the amino nitrogen, or phenolic oxygen, e.g. substituted and unsubstituted alkyl and aryl groups. Again, peroxide-compatible salts thereof are suitable for use herein.

Examples of aromatic amines, phenols and derivatives thereof are compounds of the general formulas (IV) and (V) below:



OR



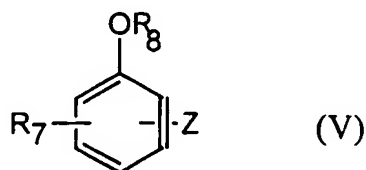
wherein Z is hydrogen, C₁ and C₃ alkyl, halogen (e.g. fluorine, chlorine, bromine or iodine) nitro,



-COOM or SO₃M, (where M is hydrogen or an alkali or alkaline earth metal, ammonium or substituted ammonium wherein one or more hydrogens on the ammonium ion is replaced with a 1 to 3 carbon atom alkyl or hydroxyalkyl radical), wherein R₁ and R₂ are the same or different and are selected from the group consisting of hydrogen, C₁ to C₄ alkyl or alkenyl and C₆ to C₉ aryl, alkaryl or aralkyl and R₇ is hydrogen, C₁ to C₄ unsubstituted or substituted alkyl or alkenyl wherein the substituents are selected from those designated as Z above or C₆ to C₉ unsubstituted or substituted aryl, alkaryl or aralkyl wherein the substituents are selected from those defined as Z above and wherein X is as defined in formula (I).

Specific examples of formula (IV) compounds are:

aniline, p-chloroaniline, p-fluoroaniline, p-nitroaniline, p-aminobenzaldehyde, p-aminobenzoic acid, sodium-p-aminobenzoate, lithium-p-aminobenzoate, calcium di-p-aminobenzoate, ammonium-p-aminobenzoate, trimethylammonium-p-aminobenzoate, tri(2-hydroxyethyl)-p-aminobenzoate, p-aminobenzenesulfonic acid, potassium p-aminobenzenesulfonate, N-methylaniline, N-propyl-N-phenylaniline, N-methyl-N-2-propenylaniline, N-benzylaniline, N-(2-ethylphenyl)aniline, 4-methylaniline, 4-(2-bromoethyl)aniline, 2-(2-nitroethyl)aniline, (4-aminophenyl)acetaldehyde, (4-aminophenyl)acetic acid, 4-(2-propenyl)aniline acetate, 4-(3-bromo-2-propenyl)aniline, 4-phenylaniline chloroacetate, 4-(3-chlorophenyl)aniline, 4-benzylaniline, 4-(4-iodobenzyl)aniline, 4-(3-ethylphenyl)aniline, 4-(2-chloro-4-ethylphenyl)aniline.



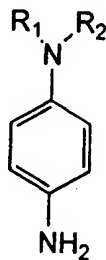
wherein Z and R₇ are defined as in formula (IV) and R₈ is hydrogen or C₁ to C₄ substituted or unsubstituted alkyl or alkenyl wherein the substituents are selected from those defined as Z in formula (IV).

Specific examples of formula (V) compounds are:

phenol, p-chlorophenol, p-nitrophenol, p-hydroxybenzaldehyde, p-hydroxybenzoic acid, p-hydroxybenzenesulfonic acid, ethylphenyl ether, 2-chloroethylphenyl ether, 2-nitroethylphenyl ether, phenoxyacetaldehyde, phenoxyacetic acid, 3-phenoxy-1-propene, 3-phenoxy-2-nitro-1-propene, 3-phenoxy-2-bromo-1-propene, 4-propylphenol, 4-(3-bromopropyl)phenol, 2-(2-nitroethyl)phenol, (4-hydroxyphenyl)acetaldehyde, (4-hydroxyphenyl)acetic acid, 4-(2-propenyl)phenol, 4-phenylphenol, 4-benzylphenol, 4-(3-fluoro-2-propenyl)phenol, 4-(4-chlorobenzyl)phenol, 4-(3-ethylphenyl)phenol, 4-(2-chloro-3-ethylphenyl)phenol, 2,5-xlenol, 2,5-diaminopyridine, 2-hydroxy-5-aminopyridine, 2-amino-3-hydroxy pyridine, tetraaminopyrimidine, 1,2,4-trihydroxybenzene, 1,2,4-trihydroxy-5-(C₁-C₆-alkyl)benzene, 1,2,3-trihydroxybenzene, 4-

aminoresorcinol, 1,2-dihydroxybenzene, 2-amino-1,4-dihydroxybenzene, 2-amino-4-methoxy-phenol, 2,4-diaminophenol, 3-methoxy-1,2-dihydroxy-benzene, 1,4-dihydroxy-2-(N,N-diethylamino)benzene, 2,5-diamino-4-methoxy-1-hydroxybenzene, 4,6-dimethoxy-3-amino-1-hydroxybenzene, 2,6-dimethyl-4-[N-(p-hydroxyphenyl)amino]-1-hydroxybenzene, 1,5-diamino-2-methyl-4-[N-(p-hydroxyphenyl)amino]benzene and salts thereof.

In preferred compositions suitable for use herein the following combination of primary intermediates and couplers are excluded:

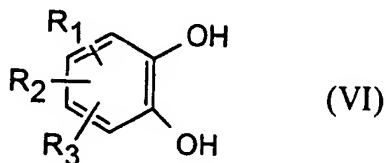


Where R_1 and R_2 are not H

in combination with m-aminophenol, resorcinol, 2-methyl-5-aminophenol, 2-methylresorcinol and mixtures thereof.

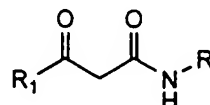
Additional primary intermediates suitable for use herein include catechol species and in particular catechol "dopa" species which includes dopa itself as well as homologs, analogs and derivatives of DOPA. Examples of suitable catechol species include cysteinyl dopa, alpha alkyl dopa having 1 to 4, preferably 1 to 2 carbon atoms in the alkyl group, epinephrine and dopa alkyl esters having 1 to 6, preferably 1 to 2 carbon atoms in the alkyl group.

In general suitable catechols are represented by formula (VI) below:

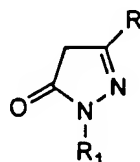


wherein R_1 , R_2 and R_3 , which may be the same or different, are electron donor or acceptor substituents selected from H, lower (C_1 - C_6) alkyl, OH, OR, COOR, NHCOR, CN, COOH, Halogen, NO_2 , CF_3 , SO_3H or NR_4R_5 , with the proviso that only one of the R_1 , R_2 or R_3 can be CN, COOH, halogen, NO_2 , CF_3 or SO_3H ; R_4 and R_5 , which may be the same or different, are H, lower (C_1 - C_6) alkyl or substituted lower (C_1 - C_6) alkyl in which the substituent may be OH, OR, NHCOR₆, NHCONH₂, NHCO₂R₆, NHCSNH₂, CN, COOH, SO_3H , SO_2NR_6 , SO_2R_6 or CO_2R_6 ; R_6 is lower (C_1 - C_6) alkyl, lower (C_1 - C_6) hydroxyalkyl phenyl linked to the nitrogen by an alkylene chain, phenyl or substituted phenyl with the substituent defined as R_1 , and R is C_1 - C_6 alkyl or C_1 - C_6 hydroxyalkyl.

Also included herein are oxidative hair coloring agents of the formula:



wherein: R_1 = substituted or unsubstituted benzene ring, tertiary-butyl, etc.; R = substituted or unsubstituted benzene ring and the formula:



wherein R = aminoalkyl, amidoalkyl, aminobenzene (substituted or unsubstituted), amidobenzene (substituted or unsubstituted), alkyl, substituted or unsubstituted benzene ring ; R_1 = substituted or unsubstituted benzene ring.

The primary intermediates can be used herein alone or in combination with other primary intermediates, and one or more can be used in combination with one or more couplers. The choice of primary intermediates and couplers will be determined by the color, shade and intensity of coloration which is desired. There are nineteen preferred primary intermediates and couplers which can be used herein, singly or in combination, to provide dyes having a variety of shades ranging from ash blonde to black; these

are: pyrogallol, resorcinol, p-toluenediamine, p-phenylenediamine, o-phenylenediamine, m-phenylenediamine, o-aminophenol, p-aminophenol, 4-amino-2-nitrophenol, nitro-p-phenylenediamine, N-phenyl-p-phenylenediamine, m-aminophenol, 2-amino-3-hydroxypyridine, 1-naphthol, N,N bis (2-hydroxyethyl)p-phenylenediamine, 4-amino-2-hydroxytoluene, 1,5-dihydroxynaphthalene, 2-methyl resorcinol and 2,4-diaminoanisole. These can be used in the molecular form or in the form of peroxide-compatible salts, as detailed above.

The primary intermediates and coupling compounds as aforementioned herein may be combined to deliver a wide variety of colors to the hair. The hair colors can vary by both depth of color and intensity of color. As hereinbefore described the compositions according to the present invention are valuable for the provision of high intensity colors. Intensity of color as defined herein means the quantity of color compound formed on and retained in the hair. In general, high intensity as defined herein means dark or deep colors such as dark red, dark brown or black etc. In accordance, with the above it is possible to formulate hair colors of varying color intensity by adjusting the initial levels of each of the oxidative dyeing materials.

For example low intensity colors such as natural blond to light brown hair shades generally comprise from about 0.001% to about 5%, preferably from about 0.1% to about 2%, more preferably from about 0.2% to about 1% by weight of coloring composition of total oxidative dyeing agents and may be achieved by the combination of primary intermediates such as 1,4-diamino-benzene, 2,5-diamino toluene, 2,5-diamino-anisole, 4-aminophenol, 2,5-diamino-benzyl alcohol and 2-(2',5'-diamino)phenylethanol with couplers such as resorcinol, 2-methyl resorcinol or 4-chloro resorcinol.

Similarly combination of the above primary intermediates with couplers, such as, 5-amino-2-methyl phenol and 1,3-diamino-benzene derivatives such as 2,4-diamino-anisole at levels of from about 0.5% to about 1% of total dyeing agents can lead to medium intensity red colors. High intensity colors such as blue to blue-violet hair shades can be produced by the combination of the above primary intermediates with couplers such as 1,3-

diamino-benzene or its derivatives such as 2,5-diamino-toluene at levels of from about 1% to about 6% by weight of composition of total dyeing agents. Black hair colors can be obtained by combining the aforementioned primary intermediates with couplers such as 1,3-diaminobenzene or its derivatives

However considerations have been raised against the physiological compatibility of para-amino phenol which is commonly used to impart red colors to the hair. Similarly, the physiological compatibility of some of the agents favoured for the production of black color such as paraphenylene diamine (PPD) has been called into question. Thus a need exists for oxidative hair coloring compositions which have an improved safety profile and in particular oxidative hair compositions for the delivery of dark colors i.e. high color intensity dyes, which have an improved safety profile. As discussed herein before, the low pH compositions of the present invention provide excellent hair coloring attributes in combination with reduced levels of hair damage and skin staining and/or irritation.

As such the compositions according to the present invention are valuable for the delivery of improved hair condition attributes in combination with good initial color development and consistency and improved wash fastness over time in addition to having reduced levels of hair damage and skin irritation and/or staining.

Non-oxidative and other dyes

The hair coloring compositions of the present invention may, in addition to the essential oxidative hair coloring agents, optionally include non-oxidative and other dye materials. Optional non-oxidative and other dyes suitable for use in the hair coloring compositions and processes according to the present invention include both semi-permanent, temporary and other dyes. Non-oxidative dyes as defined herein include the so-called 'direct action dyes', metallic dyes, metal chelate dyes, fibre reactive dyes and other synthetic and natural dyes. Various types of non-oxidative dyes are detailed in: 'Chemical and Physical Behaviour of Human Hair' 3rd Ed. by Clarence Robbins (pp250-259); 'The Chemistry and Manufacture

of Cosmetics'. Volume IV. 2nd Ed. Maisson G. De Navarre at chapter 45 by G.S. Kass (pp841-920); 'cosmetics: Science and Technology' 2nd Ed., Vol. II Balsam Sagarin, Chapter 23 by F.E. Wall (pp 279-343); 'The Science of Hair Care' edited by C. Zviak, Chapter 7 (pp 235-261) and 'Hair Dyes', J.C. Johnson, Noyes Data Corp., Park Ridge, U.S.A. (1973), (pp 3-91 and 113-139).

Direct action dyes which do not require an oxidative effect in order to develop the color, are also designated hair tints and have long been known in the art. They are usually applied to the hair in a base matrix which includes surfactant material. Direct action dyes include nitro dyes such as the derivatives of nitroamino benzene or nitroaminophenol; disperse dyes such as nitroaryl amines, aminoanthraquinones or azo dyes; anthraquinone dyes, naphthoquinone dyes; basic dyes such as Acridine Orange C.I. 46005.

Nitrodyes are added to dyeing compositions to enhance colour of colorant and to add suitable aesthetic colour to the dye mixture prior to application.

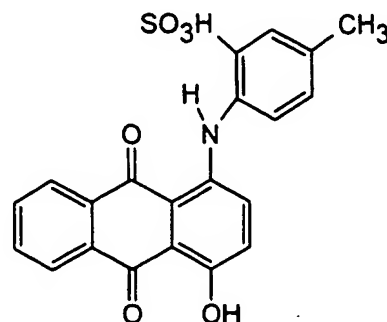
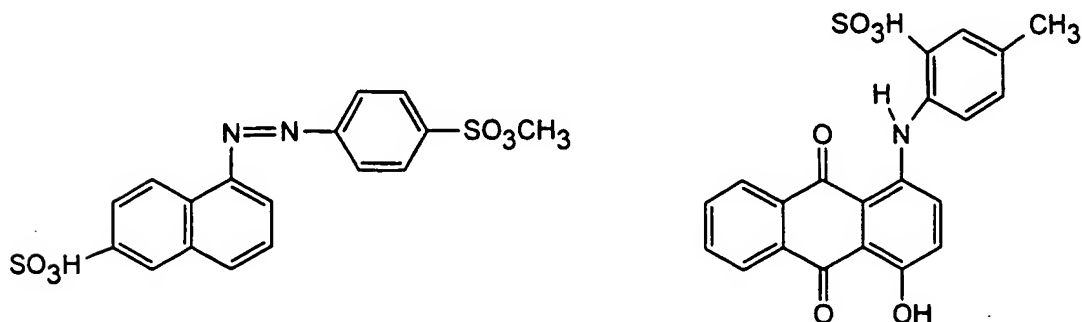
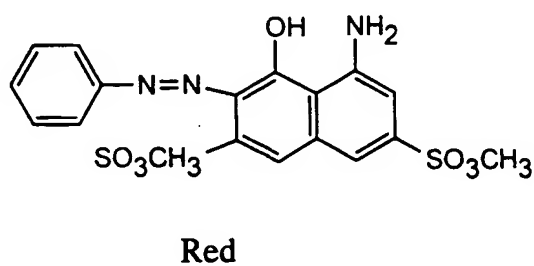
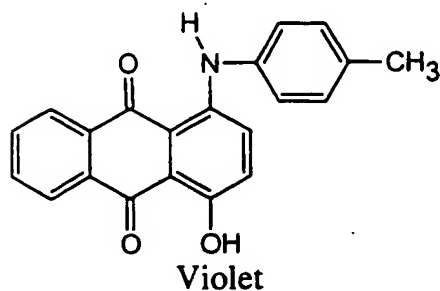
Further examples of direct action dyes include the Arianor dyes basic brown 17, C.I.(color index) - no. 12,251; basic red 76, C.I. - 12,245; basic brown 16, C.I. - 12,250; basic yellow 57, C.I. - 12,719 and basic blue 99, C.I. - 56,059 and further direct action dyes such as acid yellow 1, C.I. - 10,316 (D&C yellow no.7); acid yellow 9, C.I. - 13,015; basic violet C.I. - 45,170; disperse yellow 3, C.I. - 11,855; basic yellow 57, C.I. - 12,719; disperse yellow 1, C.I. - 10,345; basic violet 1, C.I. - 42,535, basic violet 3, C.I. - 42,555; greenish blue, C.I. - 42090 (FD&C Blue no.1); yellowish red, C.I.-14700 (FD&C red no.4); yellow, C.I.19140 (FD&C yellow no5); yellowish orange, C.I.15985 (FD&C yellow no.6); bluish green, C.I.42053 (FD&C green no.3); yellowish red, C.I.16035 (FD&C red no.40); bluish green, C.I.61570 (D&C green no.3); orange, C.I.45370 (D&C orange no.5); red, C.I.15850 (D&C red no.6); bluish red, C.I.15850(D&C red no.7); slight bluish red, C.I.45380(D&C red no.22); bluish red, C.I.45410(D&C red no.28); bluish red, C.I.73360(D&C red no.30); reddish purple, C.I.17200(D&C red no.33); dirty blue red, C.I.15880(D&C red no.34); bright yellow red, C.I.12085(D&C red no.36); bright orange, C.I.15510(D&C orange

no.4); greenish yellow, C.I.47005(D&C yellow no.10); bluish green, C.I.59040(D&C green no.8); bluish violet, C.I.60730(Ext. D&C violet no.2); greenish yellow, C.I.10316(Ext. D&C yellow no.7);

Fibre reactive dyes include the Procion (RTM), Drimarene (RTM), Cibacron (RTM), Levafix (RTM) and Remazol (RTM) dyes available from ICI, Sandoz, Ciba-Geigy, Bayer and Hoechst respectively.

Natural dyes and vegetable dyes as defined herein include henna (*Lawsonia alba*), camomile (*Matricaria chamomila* or *Anthemis nobilis*), indigo, logwood and walnut hull extract.

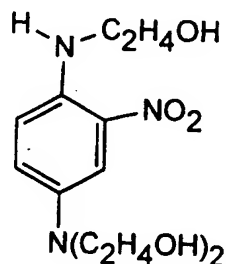
Temporary hair dyes, or hair coloring rinses, are generally comprised of dye molecules which are too large to diffuse into the hair shaft and which act on the exterior of the hair. They are usually applied via a leave-in procedure in which the dye solution is allowed to dry on the hair surface. As such these dyes are typically less resistant to the effects of washing and cleaning the hair with surface active agents and are washed off of the hair with relative ease. Any temporary hair dye may suitably be used in the compositions of the invention and examples of preferred temporary hair dyes are illustrated below.



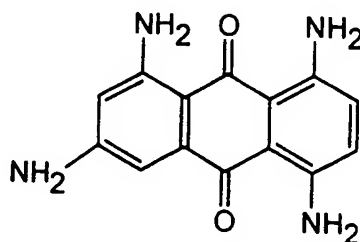
Yellow

Blue-Violet

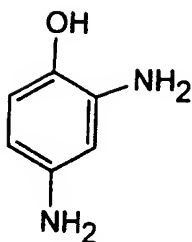
Semi-permanent hair dyes are dyes which are generally smaller in size and effect to temporary hair rinses but are generally larger than permanent (oxidative) dyes. Typically, semi-permanent dyes act in a similar manner to oxidative dyes in that they have the potential to diffuse into the hair shaft. However, semi-permanent dyes are generally smaller in size than the aforementioned conjugated oxidative dye molecules and as such are pre-disposed to gradual diffusion out of the hair again. Simple hair washing and cleaning action will encourage this process and in general semi-permanent dyes are largely washed out of the hair after about 5 to 8 washes. Any semi-permanent dye system may be suitably used in the compositions of the present invention. Suitable semi-permanent dyes for use in the compositions of the present invention are HC Blue 2, HC Yellow 4, HC Red 3, Disperse Violet 4, Disperse Black 9, HC Blue 7, HC Yellow 2, Disperse Blue 3, Disperse violet 1 and mixtures thereof. Examples of semi-permanent dyes are illustrated below:



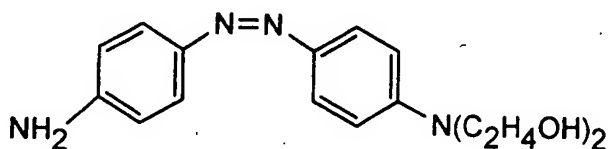
Blue



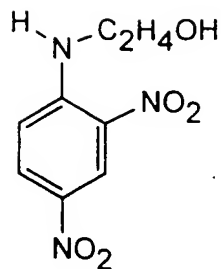
Blue



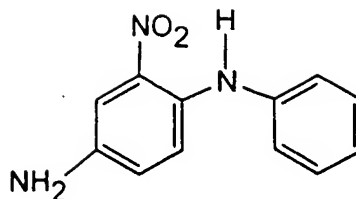
Yellow



Yellow



Red



Red

Typical semi-permanent dye systems incorporate mixtures of both large and small color molecules. As the size of the hair is not uniform from root to tip the small molecules will diffuse both at the root and tip, but will not be retained within the tip, while the larger molecules will be generally only be able to diffuse into the ends of the hair. This combination of dye molecule size is used to help give consistent color results from the root to the tip of the hair both during the initial dyeing process and during subsequent washing.

Buffering Agents

The coloring compositions of the present invention have a pH in the range of from about 1 to about 4.5, preferably from about 1.5 to about 4.5, more preferably from about 2 to about 4.4, most preferably from about 3.6 to about 4.3 and especially from about 3.8 to about 4.2.

As herein before described the pH of the preferred coloring compositions of the present invention are maintained within the desired pH range via the action of the inorganic peroxygen oxidising agent. However, if so desired, the compositions may contain one or more optional buffering agents and/or hair swelling agents (HSAs). Several different pH modifiers can be used to adjust the pH of the final composition or any constituent part thereof.

This pH adjustment can be effected by using well known acidifying agents in the field of treating keratinous fibres, and in particular human hair, such as inorganic and organic acids such as hydrochloric acid, tartaric acid, citric acid, succinic acid, phosphoric acid and carboxylic or

sulphonic acids such as ascorbic acid, acetic acid, lactic acid, sulphuric acid, formic acid, ammonium sulphate and sodium dihydrogenphosphate /phosphoric acid, disodium hydrogenphosphate /phosphoric acid, potassium chloride /hydrochloric acid, potassium dihydrogen phthalate/ hydrochloric acid, sodium citrate / hydrochloric acid, potassium dihydrogen citrate /hydrochloric acid, potassium dihydrogencitrate/ citric acid, sodium citrate / citric acid, sodium tartarate/ tartaric acid, sodium lactate/ lactic acid, sodium acetate/ acetic acid, disodium hydrogenphosphate/ citric acid and sodium chloride/ glycine / hydrochloric acid, succinic acid and mixtures thereof.

Examples of alkaline buffering agents are ammonium hydroxide, ethylamine, dipropylamine, triethylamine and alkanediamines such as 1,3-diaminopropane, anhydrous alkaline alkanolamines such as, mono or di-ethanolamine, preferably those which are completely substituted on the amine group such as dimethylaminoethanol, polyalkylene polyamines such as diethylenetriamine or a heterocyclic amine such as morpholine as well as the hydroxides of alkali metals, such as sodium and potassium hydroxide, hydroxides of alkali earth metals, such as magnesium and calcium hydroxide, basic amino acids such as L-arginine, lysine, alanine, leucine, iso-leucine, oxylysine and histidine and alkanolamines such as dimethylaminoethanol and aminoalkylpropanediol and mixtures thereof. Also suitable for use herein are compounds that form HCO_3^- by dissociation in water (hereinafter referred to as 'ion forming compounds'). Examples of suitable ion forming compounds are Na_2CO_3 , NaHCO_3 , K_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$, NH_4HCO_3 , CaCO_3 and $\text{Ca}(\text{HCO}_3)$ and mixtures thereof.

Preferred for use herein as buffering agents are organic and inorganic acids having a first pKa below pH 6, and their conjugate bases. As defined herein, first pKa means, the negative logarithm (to the base 10) of the equilibrium constant, K, where K is the acid dissociation constant. Suitable organic and inorganic acids for use herein are: aspartic, maleic, tartaric, glutamic, glycolic, acetic, succinic, salicylic, formic, benzoic, malic, lactic, malonic, oxalic, citric, phosphoric acid and mixtures thereof. Particularly preferred are acetic, succinic, salicylic and phosphoric acids and mixtures thereof.

The low pH coloring compositions according to the present invention, may, as will be described later herein, be comprised of a final solution containing both peroxide and a oxidative hair coloring agents which have been admixed prior to application to the hair or a single component system. As such, the compositions according to the present invention may comprise coloring kits of a number of separate components.

In oxidising and coloring kits comprising a portion of inorganic peroxygen oxidising agent, such as hydrogen peroxide, which may be present in either solid or liquid form, a buffering agent solution can be used to stabilise hydrogen peroxide. Since hydrogen peroxide is stable in the pH range from 2 to 4, it is necessary to use a buffering agent having a pH within this range. Dilute acids are suitable hydrogen peroxide buffering agents.

In oxidising and coloring kits comprising an oxidising agent (which may be in solid or liquid form) in combination with one or more coloring agents, a buffering agent capable of maintaining a solution pH in the range of from about 1 to about 4.5, preferably from about 1.5 to about 4.5, more preferably from about 2 to about 4.4, most preferably from about 3.6 to about 4.3 and especially from about 3.8 to about 4.2. As such it is necessary to use a buffering agent having a pH within this range.

Catalyst

The coloring compositions herein may optionally contain a transition metal containing catalyst for the inorganic peroxygen oxidising agents and the, optional, preformed peroxy acid oxidising agent(s). One suitable type of catalyst is a catalyst system comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminium cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra

(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in US-A-4,430,243.

Other types of suitable catalysts include the manganese-based complexes disclosed in US-A-5,246,621 and US-A-5,244,594. Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_2$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, and mixtures thereof. Others are described in EP-A-0,549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

For examples of suitable catalysts see US-A-4,246,612 and US-A-5,227,084. See also US-A-5,194,416 which teaches mononuclear manganese (IV) complexes such as $\text{Mn}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})(\text{OCH}_3)_3(\text{PF}_6)$. Still another type of suitably catalyst, as disclosed in US-A-5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $\text{N}_4\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{N}_4)^+$ and $[\text{Bipy}_2\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{bipy}_2](\text{ClO}_4)_3$.

Further suitable catalysts are described, for example, in EP-A-0,408,131 (cobalt complex catalysts), EP-A-0,384,503, and EP-A-0,306,089 (metallo-porphyrin catalysts), US-A-4,728,455 (manganese/multidentate ligand catalyst), US-A-4,711,748 and EP-A-0,224,952, (absorbed manganese on aluminosilicate catalyst), US-A-4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), US-A-4,626,373 (manganese/ligand catalyst), US-A-4,119,557 (ferric complex catalyst), DE-A-2,054,019 (cobalt chelant catalyst) CA-A-866,191 (transition metal-containing salts), US-A-4,430,243 (chelants with manganese cations and non-catalytic metal cations), and US-A-4,728,455 (manganese gluconate catalysts).

Heavy metal ion sequestrant

The coloring compositions of the invention may contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate or scavenge) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper. Such sequestering agents are valuable in hair coloring compositions as herein described for the delivery of controlled oxidising action as well as for the provision of good storage stability of the hair coloring products.

Heavy metal ion sequestrants are generally present at a level of from about 0.005% to about 20%, preferably from about 0.01% to about 10%, more preferably from about 0.05% to about 2% by weight of the compositions.

Various sequestering agents, including the amino phosphonates, available as Dequest (RTM) from Monsanto, the nitriloacetates, the hydroxyethyl-ethylene triamines and the like are known for such use. Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy diphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

Preferred biodegradable non-phosphorous heavy metal ion sequestrants suitable for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenetriamine pentaacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutamic acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-

disuccinic acid (EDDS). see US-A-4,704,233, or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequesterant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N,N'-diglutamic acid (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS) are also suitable.

The heavy metal ion sequestering agents of the present invention may be used in their alkali or alkaline earth metal salts.

Thickeners

The coloring compositions of the present invention may additionally include a thickener at a level of from about 0.05% to about 20%, preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 5% by weight. Thickening agents suitable for use in the compositions herein are selected from oleic acid, cetyl alcohol, oleyl alcohol, sodium chloride, cetearyl alcohol, stearyl alcohol, synthetic thickeners such as Carbopol, Aculyn and Acrosyl and mixtures thereof. Preferred thickeners for use herein are Aculyn 22 (RTM), steareth-20

methacrylate copolymer; Aculyn 44 (RTM) ,polyurethane resin and Acusol 830 (RTM), acrylates copolymer which are available from Rohm and Haas, Philadelphia, PA, USA. Additional thickening agents suitable for use herein include sodium alginate or gum arabic, or cellulose derivatives, such as methyl cellulose or the sodium salt of carboxymethylcellulose or acrylic polymers.

Diluent

Water is the preferred diluent for the compositions according to the present invention. However, the compositions according to the present invention may include one or more solvents as additional diluent materials. Generally, solvents suitable for use in the coloring compositions of the present invention are selected to be miscible with water and innocuous to the skin. Solvents suitable for use as additional diluents herein include C₁-C₂₀ mono- or polyhydric alcohols and their ethers, glycerine, with monohydric and dihydric alcohols and their ethers preferred. In these compounds, alcoholic residues containing 2 to 10 carbon atoms are preferred. Thus, a preferred group includes ethanol, isopropanol, n-propanol, butanol, propylene glycol, ethylene glycol monoethyl ether, and mixtures thereof. Water is the preferred principal diluent in the compositions according to the present invention. Principal diluent, as defined herein, means, that the level of water present is higher than the total level of any other diluents.

The diluent is present at a level preferably of from about 5% to about 99.98%, preferably from about 15% to about 99.5%, more preferably at least from about 30% to about 99%, and especially from about 50% to about 98% by weight of the compositions herein.

Enzyme

A further additional material useful in the hair coloring compositions according to the present invention is one or more enzymes.

Suitable enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139 incorporated herein by reference.

Peroxidases are haemoproteins specific for peroxide, but using a wide range of substances as donors. Catalase which decomposes peroxide, is included here in view of the fact that it is generally similar in structure and properties and is able to bring about certain oxidations by H_2O_2 . The decomposition of H_2O_2 can be regarded as the oxidation of one molecule by the other. It is widespread in aerobic cells and may have some more important function. The coenzyme peroxidases are not haemoproteins and one at least is a flavoprotein. Other flavoproteins such as xanthine oxidase will also use H_2O_2 among other acceptors, and the coenzyme peroxidases resemble these rather than the classical peroxidases in not being specific for H_2O_2 . Suitable peroxidases for the compositions of the present invention include horseradish peroxidase, Japanese radish peroxidase, cow's milk peroxidase, rat liver peroxidase, linginase and haloperoxidase such as chloro- and bromo-peroxidase.

Enzymes are optionally incorporated at levels sufficient to provide up to about 50 mg by weight, more typically about 0.01mg to about 10 mg of active enzyme per gramm of the hair treatment composition of the invention. Stated otherwise the peroxidase enzyme may be incorporated into the compositions in accordance with the invention at a level of from about 0.0001% to about 5%, preferably from about 0.001% to about 1%, more preferably from about 0.01% to about 1% active enzyme by weight of the composition.

Commercially available protease enzymes include those sold under the trade names Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated

into the compositions in accordance with the invention at a level of from 0.0001 % to 4 % active enzyme by weight of the composition.

Amylases include, for example, α -amylases obtained from a special strain of *B licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001 % to 2 % active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001 % to 2 % by weight, preferably 0.001 % to 1 % by weight, most preferably from 0.001 % to 0.5 % by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of *Humicola* sp., *Thermomyces* sp. or *Pseudomonas* sp. including *Pseudomonas pseudoalcaligenes* or *Pseudomonas fluorescens*. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from *Pseudomonas pseudoalcaligenes*, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from *Humicola lanuginosa* and expressing the gene in *Aspergillus oryza*, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

Surfactant Materials

The compositions of the present invention can additionally contain a surfactant system. Suitable surfactants for inclusion in the compositions of the invention generally have a lipophilic chain length of from about 8 to

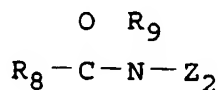
about 22 carbon atoms and can be selected from anionic, cationic, nonionic, amphoteric, zwitterionic surfactants and mixtures thereof.

(i) Anionic Surfactants

Anionic surfactants suitable for inclusion in the compositions of the invention include alkyl sulphates, ethoxylated alkyl sulphates, alkyl glyceryl ether sulfonates, methyl acyl taurates, fatty acyl glycinate, N-acyl glutamates, acyl isethionates, alkyl sulfosuccinates, alkyl ethoxysulphosuccinates, alpha-sulfonated fatty acids, their salts and/or their esters, alkyl ethoxy carboxylates, alkyl phosphate esters, ethoxylated alkyl phosphate esters, alkyl sulphates, acyl sarcosinates and fatty acid/protein condensates, and mixtures thereof. Alkyl and/or acyl chain lengths for these surfactants are C₁₂-C₂₂, preferably C₁₂-C₁₈ more preferably C₁₂-C₁₄.

(ii) Nonionic Surfactants

The compositions of the invention can also comprise water-soluble nonionic surfactant(s). Surfactants of this class include C₁₂-C₁₄ fatty acid mono- and diethanolamides, sucrose polyester surfactants and polyhydroxy fatty acid amide surfactants having the general formula below.

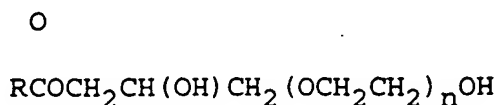


The preferred N-alkyl, N-alkoxy or N-aryloxy, polyhydroxy fatty acid amide surfactants according to the above formula are those in which R₈ is C₅-C₃₁ hydrocarbyl, preferably C₆-C₁₉ hydrocarbyl, including straight-chain and branched chain alkyl and alkenyl, or mixtures thereof and R₉ is typically hydrogen, C₁-C₈ alkyl or hydroxyalkyl, preferably methyl, or a group of formula -R¹-O-R² wherein R¹ is C₂-C₈ hydrocarbyl including straight-chain, branched-chain and cyclic (including aryl), and is preferably C₂-C₄ alkylene, R² is C₁-C₈ straight-chain, branched-chain and cyclic hydrocarbyl including aryl and oxyhydrocarbyl, and is preferably C₁-C₄ alkyl, especially methyl, or phenyl. Z₂ is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of glyceraldehyde) or at least 3 hydroxyls (in the case

of other reducing sugars) directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z_2 preferably will be derived from a reducing sugar in a reductive amination reaction, most preferably Z_2 is a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilised as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z_2 . It should be understood that it is by no means intended to exclude other suitable raw materials. Z_2 preferably will be selected from the group consisting of $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$, $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{H}$, $\text{CH}_2(\text{CHOH})_2(\text{CHOR}')\text{CHOH}-\text{CH}_2\text{OH}$, where n is an integer from 1 to 5, inclusive, and R' is H or a cyclic mono- or polysaccharide, and alkoxyated derivatives thereof. As noted, most preferred are glycityls wherein n is 4, particularly $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$.

The most preferred polyhydroxy fatty acid amide has the formula $\text{R}_8(\text{CO})\text{N}(\text{CH}_3)\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}$ wherein R_8 is a C6-C19 straight chain alkyl or alkenyl group. In compounds of the above formula, $\text{R}_8\text{-CO-N}<$ can be, for example, cocoamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmiamide, tallowamide, etc.

Suitable oil derived nonionic surfactants for use herein include water soluble vegetable and animal-derived emollients such as triglycerides with a polyethyleneglycol chain inserted; ethoxylated mono and di-glycerides, polyethoxylated lanolins and ethoxylated butter derivatives. One preferred class of oil-derived nonionic surfactants for use herein have the general formula below:



wherein n is from about 5 to about 200, preferably from about 20 to about 100, more preferably from about 30 to about 85, and wherein R comprises

an aliphatic radical having on average from about 5 to 20 carbon atoms, preferably from about 7 to 18 carbon atoms.

Suitable ethoxylated oils and fats of this class include polyethyleneglycol derivatives of glyceryl cocoate, glyceryl caproate, glyceryl caprylate, glyceryl tallowate, glyceryl palmate, glyceryl stearate, glyceryl laurate, glyceryl oleate, glyceryl ricinoleate, and glyceryl fatty esters derived from triglycerides, such as palm oil, almond oil, and corn oil, preferably glyceryl tallowate and glyceryl cocoate.

Preferred for use herein are polyethyleneglycol based polyethoxylated C₉-C₁₅ fatty alcohol nonionic surfactants containing an average of from about 5 to about 50 ethyleneoxy moieties per mole of surfactant.

Suitable polyethylene glycol based polyethoxylated C₉-C₁₅ fatty alcohols suitable for use herein include C₉-C₁₁ Pareth-3, C₉-C₁₁ Pareth-4, C₉-C₁₁ Pareth-5, C₉-C₁₁ Pareth-6, C₉-C₁₁ Pareth-7, C₉-C₁₁ Pareth-8, C₁₁-C₁₅ Pareth-3, C₁₁-C₁₅ Pareth-4, C₁₁-C₁₅ Pareth-5, C₁₁-C₁₅ Pareth-6, C₁₁-C₁₅ Pareth-7, C₁₁-C₁₅ Pareth-8, C₁₁-C₁₅ Pareth-9, C₁₁-C₁₅ Pareth-10, C₁₁-C₁₅ Pareth-11, C₁₁-C₁₅ Pareth-12, C₁₁-C₁₅ Pareth-13 and C₁₁-C₁₅ Pareth-14. PEG 40 hydrogenated castor oil is commercially available under the tradename Cremophor (RTM) from BASF. PEG 7 glyceryl cocoate and PEG 20 glyceryl laurate are commercially available from Henkel under the tradenames Cetiol (RTM) HE and Lamacit (RTM) GML 20 respectively. C₉-C₁₁ Pareth-8 is commercially available from Shell Ltd under the tradename Dobanol (RTM) 91-8. Particularly preferred for use herein are polyethylene glycol ethers of cetyl alcohol such as Cetareth 25 which is available from BASF under the trade name Cremaphor A25.

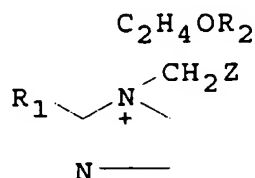
Also suitable for use herein are nonionic surfactants derived from composite vegetable fats extracted from the fruit of the Shea Tree (*Butyrospermum Karkii* Kotschy) and derivatives thereof. Similarly, ethoxylated derivatives of Mango, Cocoa and Illipe butter may be used in compositions according to the invention. Although these are classified as ethoxylated nonionic surfactants it is understood that a certain proportion may remain as non-ethoxylated vegetable oil or fat.

Other suitable oil-derived nonionic surfactants include ethoxylated derivatives of almond oil, peanut oil, rice bran oil, wheat germ oil, linseed oil, jojoba oil, oil of apricot pits, walnuts, palm nuts, pistachio nuts, sesame seeds, rapeseed, cade oil, corn oil, peach pit oil, poppyseed oil, pine oil, castor oil, soybean oil, avocado oil, safflower oil, coconut oil, hazelnut oil, olive oil, grapeseed oil, and sunflower seed oil.

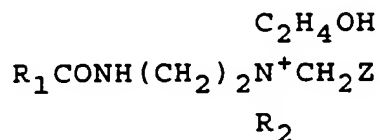
(iii) Amphoteric Surfactants

Amphoteric surfactants suitable for use in the compositions of the invention include:

(a) imidazolinium surfactants of formula (VII)

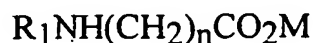


wherein R₁ is C₇-C₂₂ alkyl or alkenyl, R₂ is hydrogen or CH₂Z, each Z is independently CO₂M or CH₂CO₂M, and M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium; and/or ammonium derivatives of formula (VIII)

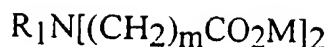


wherein R₁, R₂ and Z are as defined above;

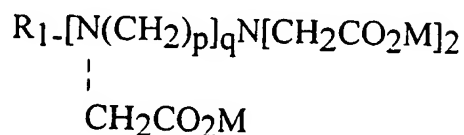
(b) aminoalkanoates of formula (IX)



iminodialkanoates of formula (X)



and iminopolyalkanoates of formula (XI)



wherein n, m, p, and q are numbers from 1 to 4, and R₁ and M are independently selected from the groups specified above; and

(c) mixtures thereof.

Suitable amphoteric surfactants of type (a) are marketed under the trade name Miranol and Empigen and are understood to comprise a complex mixture of species. Traditionally, the Miranols have been described as having the general formula (VII), although the CTFA Cosmetic Ingredient Dictionary, 3rd Edition indicates the non-cyclic structure (VIII) while the 4th Edition indicates yet another structural isomer in which R₂ is O-linked rather than N-linked. In practice, a complex mixture of cyclic and non-cyclic species is likely to exist and both definitions are given here for sake of completeness. Preferred for use herein, however, are the non-cyclic species.

Examples of suitable amphoteric surfactants of type (a) include compounds of formula XII and/or XIII in which R₁ is C₈H₁₇ (especially iso-capryl), C₉H₁₉ and C₁₁H₂₃ alkyl. Especially preferred are the compounds in which R₁ is C₉H₁₉, Z is CO₂M and R₂ is H; the compounds in which R₁ is C₁₁H₂₃, Z is CO₂M and R₂ is CH₂CO₂M; and the compounds in which R₁ is C₁₁H₂₃, Z is CO₂M and R₂ is H.

In CTFA nomenclature, materials suitable for use in the present invention include cocoamphocarboxypropionate, cocoamphocarboxy propionic acid, and especially cocoamphoacetate and cocoamphodiacetate (otherwise referred to as cocoamphocarboxyglycinate). Specific commercial products

include those sold under the trade names of Ampholak 7TX (sodium carboxy methyl tallow polypropyl amine), Empigen CDL60 and CDR 60 (Albright & Wilson), Miranol H2M Conc. Miranol C2M Conc. N.P., Miranol C2M Conc. O.P., Miranol C2M SF, Miranol CM Special (Rhône-Poulenc); Alkateric 2CIB (Alkaril Chemicals); Amphoterger W-2 (Lonza, Inc.); Monateric CDX-38, Monateric CSH-32 (Mona Industries); Rewoteric AM-2C (Rewo Chemical Group); and Schercotic MS-2 (Scher Chemicals). Further examples of amphoteric surfactants suitable for use herein include Octoxynol-1 (RTM), polyoxyethylene (1) octylphenyl ether; Nonoxynol-4 (RTM), polyoxyethylene (4) nonylphenyl ether and Nonoxynol-9, polyoxyethylene (9) nonylphenyl ether.

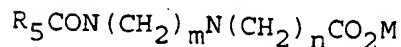
It will be understood that a number of commercially-available amphoteric surfactants of this type are manufactured and sold in the form of electroneutral complexes with, for example, hydroxide counterions or with anionic sulfate or sulfonate surfactants, especially those of the sulfated C₈-C₁₈ alcohol, C₈-C₁₈ ethoxylated alcohol or C₈-C₁₈ acyl glyceride types. Note also that the concentrations and weight ratios of the amphoteric surfactants are based herein on the uncomplexed forms of the surfactants, any anionic surfactant counterions being considered as part of the overall anionic surfactant component content.

Examples of preferred amphoteric surfactants of type (b) include N-alkyl polytrimethylene poly-, carboxymethylamines sold under the trade names Ampholak X07 and Ampholak 7CX by Berol Nobel and also salts, especially the triethanolammonium salts and salts of N-lauryl-beta-amino propionic acid and N-lauryl-imino-dipropionic acid. Such materials are sold under the trade name Deriphat by Henkel and Mirataine by Rhône-Poulenc.

(iv) Zwitterionic Surfactants

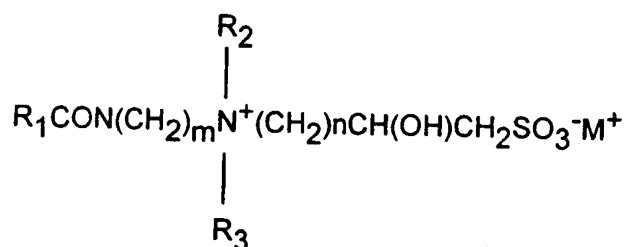
Water-soluble auxiliary zwitterionic surfactants suitable for inclusion in the compositions of the present invention include alkyl betaines of the formula $R_5R_6R_7N^+(CH_2)_nCO_2M$ and amido betaines of the formula (XII) below:

50

 R_6  R_7

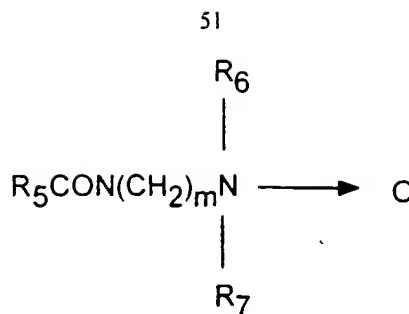
wherein R_5 is C_{11} - C_{22} alkyl or alkenyl, R_6 and R_7 are independently C_1 - C_3 alkyl, M is H , alkali metal, alkaline earth metal, ammonium or alkanolammonium, and n , m are each numbers from 1 to 4. Preferred betaines include cocoamidopropyldimethylcarboxymethyl betaine, laurylamidopropyldimethylcarboxymethyl betaine and Tego betaine (RTM).

Water-soluble auxiliary sultaine surfactants suitable for inclusion in the compositions of the present invention include alkyl sultaines of the formula (XIII) below:



wherein R_1 is C_7 to C_{22} alkyl or alkenyl, R_2 and R_3 are independently C_1 to C_3 alkyl, M is H , alkali metal, alkaline earth metal, ammonium or alkanolammonium and m and n are numbers from 1 to 4. Preferred for use herein is coco amido propylhydroxy sultaine.

Water-soluble auxiliary amine oxide surfactants suitable for inclusion in the compositions of the present invention include alkyl amine oxide $R_5R_6R_7\text{NO}$ and amido amine oxides of the formula (XIV) below:



wherein R_5 is C_{11} to C_{22} alkyl or alkenyl, R_6 and R_7 are independently C_1 to C_3 alkyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium and m is a number from 1 to 4. Preferred amine oxides include cocoamidopropylamine oxide, lauryl dimethyl amine oxide and myristyl dimethyl amine oxide.

Optional Materials

A number of additional optional materials can be added to the coloring compositions herein described each at a level of from about 0.001% to about 5%, preferably from about 0.01% to about 3%, more preferably from about 0.05% to about 2% by weight of composition. Such materials include proteins and polypeptides and derivatives thereof; water-soluble or solubilizable preservatives such as DMDM Hydantoin, Germall 115, methyl, ethyl, propyl and butyl esters of hydroxybenzoic acid, EDTA, Euxyl (RTM) K400, natural preservatives such as benzyl alcohol, potassium sorbate and bisababol, benzoic acid, sodium benzoate and 2-phenoxyethanol; antioxidants such as sodium sulphite, hydroquinone, sodium bisulphite, sodium metabisulphite and thyoglycolic acid, sodium dithionite, erythroic acid and other mercaptans; dye removers such as oxalic acid, sulphated castor oil, salicylic acid and sodium thiosulphate; H_2O_2 stabilisers such as tin compounds such as sodium stannate, stannic hydroxide and stannous octoate, acetanilide, phenacetin colloidal silica such as magnesium silicate, oxyquinoline sulphate, sodium phosphate, and tetrasodium pyrophosphate; and p -hydroxybenzoates; moisturising agents such as hyaluronic acid, chitin, and starch-grafted sodium polyacrylates such as Sanwet (RTM) IM-1000, IM-1500 and IM-2500 available from Celanese Superabsorbent Materials, Portsmouth, VA, USA and described in

US-A-4,076,663 as well as methyl cellulose, starch, higher fatty alcohols, paraffin oils, fatty acids and the like; solvents ; anti-bacterial agents such as Oxeco (phenoxy isopropanol); low temperature phase modifiers such as ammonium ion sources (e.g. $\text{NH}_4 \text{Cl}$); viscosity control agents such as magnesium sulfate and other electrolytes; quaternary amine compounds such as distearyl-, dilauryl-, di-hydrogenated beef tallow-, dimethyl ammonium chloride, dicetyldiethyl ammoniummethylsulphate, ditallowdimethyl ammonium methylsulphate, disoya dimethyl ammonium chloride and dicoco dimethyl ammonium chloride; hair conditioning agents such as silicones, higher alcohols, cationic polymers and the like; enzyme stabilisers such as water soluble sources of calcium or borate species; colouring agents; TiO_2 and TiO_2 -coated mica; perfumes and perfume solubilizers; and zeolites such as Valfour BV400 and derivatives thereof and $\text{Ca}^{2+}/\text{Mg}^{2+}$ sequestrants such as polycarboxylates, amino polycarboxylates, polyphosphonates, amino polyphosphonates etc. and water softening agents such as sodium citrate.

The present invention is represented by the following non-limiting examples. In the examples, all concentrations are on a 100% active basis and all percentages are by weight unless otherwise stated and the abbreviations have the following designations:

Oxidising agent	hydrogen peroxide
Oxidative Dye 1	para-phenylene diamine
Oxidative Dye 2	para-aminophenol
Oxidative Dye 3	meta-aminophenol
Oxidative Dye 4	2-amino-3-hydroxy pyridine
Oxidative Dye 5	4-amino-2-hydroxy toluene
Non-oxidative Dye	Basic red 76
Chelating agent	Ethylenediamine tetraaceticacid
Surfactant 1	Ceteareth-25
Surfactant 2	Cocoamidopropyl betaine
Thickener 1	Cetyl alcohol
Thickener 2	Stearyl alcohol
Antioxidant	Sodium sulphite
Buffering Agent	Acetic acid

Examples I - VII

The following are hair treatment compositions in the form of hair coloring compositions which are representative of the present invention.

<u>Ingredient</u>	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>	<u>VI</u>	<u>VII</u>
Oxidising Agent	0.7	0.7	0.7	0.7	1.0	1.5	2.5
Oxidative Dye 1	0.24	0.14	0.24	0.24	0.24	0.24	0.3
Oxidative Dye 2	0.09	0.05	0.009	0.09	-	-	0.1
Oxidative Dye 3	0.006	0.004	0.006	0.006	0.006	0.006	-
Oxidative Dye 4	0.06	0.03	0.06	0.06	0.06	0.06	0.06
Oxidative Dye 5	-	-	-	-	-	0.5	-
Non-Oxidative Dye-	-	-	-	-	0.1	-	-
Surfactant 1	1.5	1.7	1.5	1.5	1.5	-	3.0
Surfactant 2	-	-	-	-	-	1.5	-
Chelating agent	0.1	0.06	0.09	0.1	0.1	0.1	0.1
Thickener 1	2.3	2.6	2.3	2.3	2.3	2.3	2.0
Thickener 2	2.3	2.6	2.3	2.3	2.3	2.3	4.0
Antioxidant	0.1	0.06	0.1	0.1	0.1	0.1	0.1
Buffer	-	-	-	0.5	-	-	-
Water to balance						
pH	4.0	3.8	3.9	2.7	-	-	-

In the examples, water is used as the diluent. However in variations hereof water can be replaced, in part, by from about 0.5% to about 50% by weight of the total water content of the examples by diluents such as lower alcohols, e.g., ethylene glycol, ethylene glycol monoethyl ether, diethylene glycol, diethylene glycol monoethyl ether, propylene glycol, 1,3-propane diol, ethanol, isopropyl alcohol, glycerine, butoxyethanol, ethoxydiglycol, hexylene glycol, polyglyceryl-2-oleyl ether and mixtures thereof.

Experimental Methods

I Assessment of Initial Color and Color Change

The equipment used to measure both the initial color and color change on substrates (hair / skin) dyed with the low pH coloring compositions of the present invention is a Hunter Colorquest spectrophotometer. The value used to express the degree of color change on any particular substrate is Delta E (ΔE). Delta E, as defined herein, is represented by a factual sum of L, a, and b values such that:

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

and L is a measure of lightness and darkness (color intensity), wherein L = 100 is equivalent to white, and L = 0 is equivalent to black. Further, 'a' is a measure of the red and green quotients (color hues) such that positive equates to red and negative equates to green, and 'b' is a measure of the yellow and blue quotients (color hues) such that positive equates to yellow and negative equates to blue.

Hunter Colorquest measurements can be carried out on the Hunter Labscan Colorimeter which is full scanning spectrophotometer with a wavelength of from 400-700 nanometers which records the color of test hair switches (tresses) in terms of 'L', 'a' and 'b' values. The machine is set to: mode - 0/45; port size - 1 inch; view size - 1 inch; light - D65; field of view - 10°; UV lamp/filter - none. The hair is placed in a sample holder designed to hold the hair in a uniform orientation during measurement. Equivalent colorimeters can be used, but it must be ensured that the hair does not move during measurement. The hair must be spread to cover the 1 inch port during color measurement. Dots are placed on the switch holder to guide the positioning of the holder at the port. The dots are lined up with a mark on the port and readings are taken at each spot.

Eight measurements are run per switch, 4 on each side, and three switches are run per treatment.

II. Standard Hair Switch

The compositions according to the present invention can be used to color hair of all colors, types and condition. For the purposes of illustration two test hair switch types; light brown and light brown with 40% grey coverage have been tested herein. These standard hair switches can be measured in terms of their approximate L, a, b values.

	<u>L</u>	<u>a</u>	<u>b</u>
Light brown	60	9	32
40% grey light brown	35 - 37	4.5 - 5.5	11.5 - 12.7

III Hair Switch Coloring Method

To color hair, a 4 gramme switch of about 8 inch long hair is hung over a suitable container. The test coloring product is then prepared (i.e., where applicable the separate bottle components are mixed together) and about 8 grammes of product is applied directly to the test hair switch. The colorant is massaged through the hair switch for up to about 1 minute and then left on the hair switch for up to about 30 minutes. After rinsing with running water for about 1 or 2 minutes the colored hair switch is then cleansed (according to the shampoo protocol) and dried. Drying can be effected either naturally (without heat assistance) or using a drier. The color development (initial color) of the colored, cleansed, dried test hair switch can then be assessed using the Hunter Colorquest spectrophotometer.

For the delivery of a red shade (hue) to prepermed, prebleached light brown hair (having L, a, b values of approximately 60, 9 and 32) the preferred initial shade of the colored hair will have a hue value (arc tangent of (b/a)) in the range of from about 25 to about 70, more preferably from about 30 to about 65, most preferably from about 35 to about 60 and wherein the initial color intensity (L) is greater than about 10 and less than about 70, preferably greater than about 15 and less than about 65, more preferably greater than about 20 and less than about 60.

For the delivery of a brown or black shade (hue) to prepermed, prebleached light brown hair (having L, a, b values of approximately 60, 9 and 32) the preferred initial shade of the colored hair will have a hue value (arc tangent of (b/a)) of less than about 25, preferably less than about 20 and the initial color intensity (L) will be greater than about 1 and less than about 50, preferably greater than about 5 and less than about 45.

For the delivery of a light brown shade (hue) to prepermed, prebleached light brown hair (having L, a, b values of approximately 60, 9 and 32) the preferred initial shade of the colored hair will have a hue value (arc tangent of (b/a)) in the range of from about 70 up to about 110 and wherein the initial color intensity (L) will be greater than about 20 and less than about 95, preferably greater than about 25 and less than about 90.

A significant color change, as delivered via the coloring compositions according to the present invention, means a color change in terms of Delta E which is greater than about 8, preferably greater than about 10, more preferably greater than about 12, most preferably greater than about 15 and especially greater than about 20.

Hair Switch Cleansing Method

Switches of colored hair are subjected to a repeated cleansing cycle wherein the following process is repeated up to 10 times.

A 4 gramme, 8 inch test switch of colored hair is clamped over a suitable container and rinsed thoroughly for about 10 seconds using warm water (at about 100°F at about 1.5 gallons/minute pressure). Shampoo (about 0.4ml non-conditioning shampoo) can then be applied directly to the wet test switch using a syringe. After lathering the hair for about 30 seconds the hair is rinsed in running warm water for about 30 seconds. The shampoo and lathering process is then repeated with a final 60 second rinse. Excess water can be removed (squeezed) from the test switch using the fingers. The test switch is then dried either naturally, or using a pre-heated dryer

box at about 140°F (for about 30 minutes). The colored, cleansed, dried test hair switch can then be color assessed (Delta E fade).

During any single test cycle each different switch to be assessed should be tested in water of equivalent temperature, pressure level and hardness level.

Delta E fade results for prepermed, prebleached light brown hair (having L, a, b values of approximately 60, 9 and 32) which has been colored a red shade (of hue value in the range of from about 25 to about 70) are generally less than about 5.0, preferably less than about 4.5, more preferably less than about 4.0 and wherein the change in hair color, % delta E, after up to 20 washes, is less than about 20%, and preferably less than about 15%, more preferably less than about 10%.

Delta E fade results for prepermed, prebleached light brown hair (having L, a, b values of approximately 60, 9 and 32) which has been colored a brown or black shade (of hue value of less than about 25) are generally less than about 2.3, preferably less than about 2.0, more preferably less than about 1.7 and wherein the change in hair color, % delta E, after up to 20 washes, is less than about 5%, preferably less than about 4.5%, more preferably less than about 4%, most preferably less than about 3.5%.

Delta E fade results for prepermed, prebleached light brown hair (having L, a, b values of approximately 60, 9 and 32) which has been colored a light brown shade (of hue value in the range of from about 70 to about 110) are generally less than about 2.6, preferably less than about 2.3 and wherein the change in hair color, % delta E, after up to 20 washes, is less than about 15%, preferably less than about 12%, more preferably less than about 10%, most preferably less than about 8%.

In preferred compositions herein, the change in the color of the dyed hair over time (Delta E fade) is less than about 15%, preferably less than about 12%, more preferably less than about 10% and most preferably less than about 8%.

V Skin Staining Test Method

For the purposes of the present invention skin staining results are based on pig skin data.

Skin staining measurements can be made on pigs ears, preferably the ears of recently deceased pigs. The ears should not have been subject to undue heating (scalding). Hair is shaved from the most flat section of the ear to be stained. An area of at least 1cm x 5cm is pre-marked on the ear (using a permanent marker) and the ear is then cleansed with non-conditioning shampoo (0.1g/cm² at 10% dilution). After massaging in the shampoo for about 1 minute the ear is rinsed for about 30 seconds then gently patted dry by hand with a paper towel. Baseline color assessment readings (L, a, b) are then taken for the pre-marked area. The test dye is then applied to the pre-marked test area (about 0.25g/cm²) and massaged in for about 1 minute and allowed to remain on the ear for about 30 minutes. The colored ear is then rinsed with about 2 litres of tap water at about 37°C and hand dried as above. Color assessment readings (L, a, b) are then taken for the pre-marked area of the dyed ear. Total color change (Delta E) can then be calculated from the L, a, b values and expressed as relative levels of skin staining (versus the baseline color).

VI Measurement of pH

For the purposes of the present invention, as described herein, all pH measurements were carried out on a Mettler Toledo 320 pH meter. All pH measurements of dyes, oxidising agents and mixtures thereof, either singly or in combination with a suitable delivery medium, such as water and surfactant and /or thickeners, were carried out at room temperature (about 25°C). The pH of dye mixtures were measured in the form of intended use and prior to application.. A preferred delivery medium for use herein comprises an emulsion of cetareth-25 at a level of from about 1% to about 3% by weight, cetyl alcohol at a level of from about 2% to about 5% by weight and stearyl alcohol at a level of from about 2% to about 5% of solution or composition.

Experimental Data

I Initial Color and Wash Fastness

Example formula I provides improved initial color and fade resistance versus a similar composition having pH outside the scope of the present invention.

Example formula II provides improved initial color development and washfastness versus a similar high pH formula containing the same level of oxidant and up to 60% more dye.

Example formula III provides improved initial color development versus a high pH formula containing the same level of dye but more inorganic peroxygen oxidising agent.

Method of Manufacture

It is important that dyeing compositions be in a form which is easy and convenient to prepare and use by the consumer, since the oxidising agent must remain in contact with the hair for a certain period of time and not run or drip off of the hair, possibly causing eye or skin irritation.

To address the above, the coloring compositions of the present invention can be provided in both a single pack or in kit form as separately packaged components to maintain stability, and, if so desired, either mixed by the user immediately prior to application to the hair, or mixed and stored for future use, or mixed and partly used and the remainder stored for future use.

As hereinbefore described, the compositions according to the present invention may be used by the consumer as a single component package. Such a single pack would comprise a single solution at pH 1 to 4.5 containing both the inorganic peroxygen oxidising agent and the oxidative

dye precursors. The solution would be applied directly to the hair by the consumer without the need for any pretreatments or mixing thereby providing a simple, fast, easy to use, 'no-mess' hair coloring system. A further advantage of such a single component system is that it could be stored and re-used i.e., a single package could contain enough coloring composition for several applications over time.

Thus, according to a further aspect of the present invention, there is provided:

A method for coloring hair wherein a hair coloring mixture is present in a single package and applied directly to the hair and wherein the hair coloring mixture comprises:

- (a) an inorganic peroxygen oxidising agent; and
- (b) an oxidative hair coloring agent;

wherein the pH of each of (a) and (b), when in solution, is in the range of from about 1 to about 4.5 and wherein the combined mixture of (a) and (b), when in solution, has a pH in the range of from about 1 to about 4.5.

According to a still further aspect of the present invention, there is provided:

A method for coloring hair wherein a hair coloring composition is present as separately packaged components (a) and (b) and wherein the hair coloring composition comprises:

- (a) an inorganic peroxygen oxidising agent wherein the pH of a), is in the range of from about 1 to about 4.5 ; and
- (b) an oxidative hair coloring agent wherein the pH of (b), is in the range of from about 1 to about 4.5;

wherein each of (a) and (b) are stable at pHs in the range of from about 1 to about 4.5 and wherein the combined mixture of (a) and (b) is stable over time and has a pH in the range of from about 1 to about 4.5.

Alternatively the compositions according to the present invention can be packaged as follows: one component of the kit comprises an individually packaged oxidising component while further kit components could comprise coloring agent mixture and, optionally, individually packaged additional, optional, oxidising agent(s), or two separate individual packages of oxidising agent and coloring agents. In one embodiment of the present invention the oxidising component comprises a stabilised aqueous solution of an inorganic peroxygen oxidising agent, most generally hydrogen peroxide, in an amount such that the final concentration of the coloring composition for use on the hair is from about 0.05% to about 6% by weight and additional agents as herein before described. The compositions can either be mixed by the user immediately prior to application to the hair or can be applied separately. Examples of such kits are as follows:

I. A hair coloring kit is assembled comprising a single package including therein: (1) a 50 ml bottle of hydrogen peroxide (1.4% by weight of H_2O_2), and optionally buffering agents and/or stabilisers; and (2) a 50 ml bottle containing one or more oxidative hair coloring agents and, optionally, additional agents such as surfactants, stabilisers, buffering agents, antioxidants, thickeners etc. The oxidative hair coloring agents can either be admixed with the hydrogen peroxide to form the low pH dyeing system of the present invention and the resulting solution can be either applied to the hair to color it or stored for future use, or the separately packaged stable components can be stored and mixed when required.

II. A hair coloring kit as described above wherein the hydrogen peroxide containing component is applied to the hair prior to application of the oxidative hair coloring agents and additional materials to the hair.

III. Further examples of kit components for the hair coloring compositions according to the present invention include separately packaged oxidant and

oxidative hair coloring agents wherein either one or both components are present in particulate form.

Method of Use

The compositions herein described are used to color hair. The coloring compositions herein are applied to the hair for periods of from 1 minute to 60 minutes depending upon the degree of coloring required. A preferred time is between 5 minutes and 30 minutes. The coloring compositions according to the present invention can be applied to both wet and dry hair.

As hereinbefore described the coloring composition can be present as a single package, at low pH, suitable for direct application to the hair. Alternatively, the coloring composition can be present in kit form wherein one component comprises an oxidising agent and a further component comprises oxidative hair coloring agents. Hair coloring kits according to the present invention can be used to color the hair in several ways including:

- (i) the kit components are admixed to form a low pH coloring composition prior to application to the hair.
- (ii) the hair oxidising agent is applied to the hair prior to application of the oxidative hair coloring agents.
- (iii) the oxidative hair coloring agents are applied to the hair prior to application of the oxidising agent.

The products provide excellent initial hair coloring and in-use efficacy benefits including improved washfastness, color saturation and reduced hair damage at lower pH.

WHAT IS CLAIMED IS:

1. A hair coloring composition comprising:

- (a) an inorganic peroxygen oxidising agent; and
- (b) an oxidative hair coloring agent;

wherein the pH of each of (a) and (b) is in the range of from about pH 1 to 4.5 and wherein the pH of the composition is in the range of from about 1 to about 4.5 .

2. A composition according to Claim 1 wherein the pH of the composition is in the range of from about 1.5 to about 4.5, preferably from about 2 to about 4.4, more preferably from about 3.6 to about 4.3, most preferably from about 3.8 to about 4.2.
3. A composition according to Claim 1 or 2 wherein the inorganic peroxygen oxidising agent is present at a molar level of from about 0.0003 moles (per 100g of composition) to less than about 0.09 moles (per 100g of composition), preferably from about 0.0003 moles to about 0.08 moles, more preferably from about 0.0003 moles to about 0.06 moles, even more preferably from about 0.0003 moles to about 0.04 moles, most preferably from about 0.0003 moles to about 0.03 moles, especially from about 0.0003 moles to about 0.02 moles and most especially from about 0.0003 moles to about 0.015 moles (per 100g of composition).
4. A composition according to any of Claims 1 to 3 wherein the inorganic peroxygen oxidising agent is present at a level of from about 0.01% to less than about 3%, preferably from about 0.01% to about 2.5%, more preferably from about 0.01% to about 2%, even more preferably from about 0.01% to about 1%, most preferably from about 0.01% to about 0.8%, especially from about 0.01% to about 0.55% and especially from about 0.01% to about 0.5% by weight of the total composition.

5. A composition according to any of Claims 1 to 4 wherein the inorganic peroxygen oxidising agent is hydrogen peroxide.
6. A composition according to any of Claims 1 to 5 wherein the total combined level of oxidative hair coloring agent is from about 0.001% to about 5%, preferably from about 0.01% to about 4%, more preferably from about 0.1% to about 3%, most preferably from about 0.1% to about 1% by weight.
7. A composition according to any of Claims 1 to 6 wherein each oxidative hair coloring agent is present at a level of from about 0.001% to about 3%, preferably from about 0.01% to about 2% by weight.
8. A composition according to any of Claims 1 to 7 additionally comprising a preformed organic peroxy acid oxidising agent.
9. A composition according to Claim 8 wherein the preformed organic peroxy acid is present at a molar level of from about 0.0001 moles to about 0.1 moles (per 100g of composition), more preferably from about 0.001 moles to about 0.05 moles, most preferably from about 0.003 moles to about 0.04 moles and especially from about 0.004 moles to about 0.03 moles per 100g of the hair coloring composition.
10. A composition according to Claim 9 wherein the preformed organic peroxy acid is present at a level of from about 0.01% to about 8%, preferably from about 0.1% to about 6%, more preferably from about 0.2% to about 4% and most preferably from about 0.3% to about 3% by weight and wherein the weight ratio of the inorganic oxidising agent : the organic oxidising agent is in the range of from about 0.00125:1 to about 500:1, preferably from about 0.0125:1 to about 50:1.
11. A composition according to any of Claims 1 to 10 additionally comprising one or more buffering agents, preferably an organic and/or organic acid having a first pKa below pH 6, selected from: aspartic, maleic, tartaric, glutamic, glycolic, acetic, succinic,

salicylic, formic, benzoic, malic, lactic, malonic, oxalic, citric, phosphoric acid and mixtures thereof, more preferably selected from acetic, succinic, salicylic and phosphoric acids and mixtures thereof.

12. A composition according to any of Claims 1 to 11 additionally comprising one or more surfactants selected from anionic, nonionic, cationic, zwitterionic, amphoteric surfactants and mixtures thereof.
13. A composition according to any of Claims 1 to 12 additionally comprising thickening agents, stabilisers, antioxidants and/or any other cosmetically acceptable material.
14. Use of a composition according to any of Claims 1 to 13 for coloring human or animal hair.
15. A process for coloring human or animal hair wherein the hair coloring composition comprises:
 - (a) an inorganic peroxygen oxidising agent; and
 - (b) an oxidative hair coloring agent;
 - (c) a diluent suitable for application to the hair;

wherein the coloring composition has a pH of from about 1 to about 4.5 .

16. A hair coloring kit comprising an individually packaged oxidising component and an individually packaged coloring component, wherein the oxidising component comprises an aqueous solution of an inorganic peroxygen oxidising agent having a pH in the range of from about 1 to about 4.5 and the coloring component comprises an oxidative hair coloring agent, capable of delivering a solution pH in the range of from about 1 to about 4.5 wherein the pH of the combined oxidising agent and coloring components is in the range of from about 1 to about 4.5.

17. Use of a hair coloring kit according to Claim 16 for the oxidising and coloring of hair wherein the oxidising agent, oxidative hair coloring agents and additional agents are admixed prior to application to the hair.
18. A method for coloring hair wherein a hair coloring mixture is applied directly to the hair and wherein the hair coloring mixture comprises:

- (a) an inorganic peroxygen oxidising agent at a pH of from about 1 to 4.5; and
- (b) an oxidative hair coloring agent at a pH of from about 1 to 4.5;

wherein the combined mixture of (a) and (b) has a pH in the range of from about 1.5 to about 4.5, preferably from about 2 to about 4.4, more preferably from about 3.6 to about 4.3, most preferably from about 3.8 to about 4.2.

19. A hair coloring composition suitable for the delivery of a red shade comprising:
- (a) an inorganic peroxygen oxidising agent at a pH of from about 1 to 4.5; and
 - (b) an oxidative hair coloring agent at a pH of from about 1 to 4.5 ;

wherein the change in hair color, delta E, is less than about 5 after 20 washes.

20. A hair coloring composition suitable for the delivery of a light brown shade comprising:

- (a) an inorganic peroxygen oxidising agent at a pH of from about 1 to 4.5; and
- (b) an oxidative hair coloring agent at a pH of from about 1 to 4.5;

wherein the change in hair color, ΔE , is less than about 2.6 after 20 washes.

21. A hair coloring composition suitable for the delivery of a brown or black shade comprising:

- (a) an inorganic peroxygen oxidising agent at a pH of from about 1 to 4.5; and
- (b) an oxidative hair coloring agent at a pH of from about 1 to 4.5;

wherein the change in hair color, ΔE , is less than about 2.3 after 20 washes.

22. A hair coloring composition, comprising an inorganic peroxygen oxidising agent and an oxidative hair coloring agent wherein the change in hair color, ΔE , is greater than about 8, preferably greater than about 10, more preferably greater than about 12, especially greater than about 15 and most especially greater than about 20, and wherein the change in hair color over time (of the colored hair), % ΔE (fade) is less than about 15%, preferably less than about 12%, more preferably less than about 10%, and especially less than about 8% after 20 washes.

23. A process capable of delivering a red shade to hair comprising: application to the hair of a composition comprising:

- (i) an inorganic peroxygen oxidising agent; and
- (ii) an oxidative hair coloring agent;

wherein the combined mixture of (i) and (ii) has a pH in the range of from about 1 to about 4.5, preferably from about 1.5 to about 4.5, more preferably from about 2 to about 4.4, most preferably from about 3.6 to about 4.3 and especially from about 3.8 to about 4.2 and wherein the untreated hair is prepermed, prebleached light brown hair having L, a, b values of approximately 60, 9 and 32 and wherein the initial shade of the colored hair has a hue value (arc tangent of (b/a)) in the range of from about 25 to about 70, preferably from about 30 to about 65, more preferably from about 35 to about 60 and wherein the initial color intensity (L) is greater than about 10 and less than about 70, preferably greater than about 15 and less than about 65, more preferably greater than about 20 and less than about 60 and wherein the delta E fade is less than about 5.0, preferably less than about 4.5, more preferably less than about 4.0 and wherein the change in hair color, % delta E, after up to 20 washes, is less than about 20%, and preferably less than about 15%, more preferably less than about 10%.

24. A process capable of delivering a brown or black shade to hair comprising: application to the hair of a composition comprising:

- (i) an inorganic peroxygen oxidising agent; and
- (ii) an oxidative hair coloring agent and mixtures thereof;

wherein the combined mixture of (i) and (ii) has a pH in the range of from about 1 to about 4.5, preferably from about 1.5 to about 4.5, more preferably from about 2 to about 4.4, most preferably from about 3.6 to about 4.3 and especially from about 3.8 to about 4.2 and wherein the untreated hair is prepermed, prebleached light brown hair having L, a, b values of approximately 60, 9 and 32 and wherein the initial shade of the colored hair has a hue value (arc tangent of (b/a)) of less than about 25, preferably less than about 20 and wherein the initial color intensity (L) is greater than about 1 and less than about 50, preferably greater than about 5 and less than about 45 and wherein the delta E fade is less than about 2.3, preferably less than about 2.0, more preferably less than about 1.7 and wherein the change in hair color, % delta E, after up to 20 washes, is less than

about 5%, preferably less than about 4.5%, more preferably less than about 4%, most preferably less than about 3.5%.

25. A process capable of delivering a light brown shade to hair comprising: application to the hair of a composition comprising:

- (i) an inorganic peroxygen oxidising agent; and
- (ii) an oxidative hair coloring agent and mixtures thereof; and

wherein the combined mixture of (i) and (ii) has a pH in the range of from about 1 to about 4.5, preferably from about 1.5 to about 4.5, more preferably from about 2 to about 4.4, most preferably from about 3.6 to about 4.3 and especially from about 3.8 to about 4.2 and wherein the untreated hair is prepermed, prebleached light brown hair having L, a, b values of approximately 60, 9 and 32 and wherein the initial shade of the colored hair has a hue value (arc tangent of (b/a)) in the range of from about 70 up to about 110 and wherein the initial color intensity (L) is greater than about 20 and less than about 95, preferably greater than about 25 and less than about 90 and wherein the delta E fade is less than about 2.6, preferably less than about 2.3 and wherein the change in hair color, % delta E, after up to 20 washes, is less than about 15%, preferably less than about 12%, more preferably less than about 10%, most preferably less than about 8%.

26. A method for coloring hair at a pH in the range of from about 1 to about 4.5 comprising application to the hair of a composition comprising:

- (a) an inorganic peroxygen oxidising agent at a pH of from about 1 to 4.5; and
- (b) an oxidative hair coloring agent at a pH of from about 1 to 4.5;
- (c) a diluent suitable for application to the hair; and

wherein the combined pH of (a) and (b) is in the range of from about pH 1 to about pH 4.5 .

27. A method for coloring hair at a pH in the range of from about 1 to about 4.5 comprising application to the hair of a composition comprising:

- (a) an inorganic peroxygen oxidising agent at a pH of from about 1 to 4.5; and
- (b) an oxidative hair coloring agent at a pH of from about 1 to 4.5;
- (c) a diluent suitable for application to the hair; and

wherein component (b) is applied to the hair, with or without a portion of component (c), prior to application of components (a) and (c), and wherein the combined pH of (a), (b) and (c) is in the range of from about pH 1 to about pH 4.5.

28. A method for coloring hair at a pH in the range of from about 1 to about 4.5 comprising application to the hair of a composition comprising:

- (a) an inorganic peroxygen oxidising agent at a pH of from about 1 to 4.5; and
- (b) an oxidative hair coloring agent at a pH of from about 1 to 4.5;
- (c) a diluent suitable for application to the hair; and

wherein component (a) is applied to the hair, with or without a portion of component (c), prior to application of components (b) and (c), and wherein the combined pH of (a), (b) and (c) is in the range of from about pH 1 to about pH 4.5 .

29. A method for coloring hair wherein a hair coloring mixture according to Claim 1 is present in a single package and applied directly to the hair.
30. A method for coloring hair wherein a hair coloring composition according to Claim 1 is present as separately packaged components (a) and (b) wherein (a) and (b) comprise:

(a) an inorganic peroxygen oxidising agent at a molar level of from about 0.0003 moles (per 100g of composition) to less than about 0.09 moles (per 100g of composition) having a pH in the range of from about 1 to about 4.5; and

(b) an oxidative hair coloring agent at a pH of from about 1 to 4.5;

wherein each of (a) and (b) are stable at pHs in the range of from about 1 to about 4.5 and wherein the combined mixture of (a) and (b) is stable over time and has a pH in the range of from about 1 to about 4.5.

31. A hair coloring composition comprising:

(a) an inorganic peroxygen oxidising agent; and

(b) an oxidative hair coloring agent;

wherein the pH of each of (a) and (b) is in the range of from about 1 to about 4.5, wherein the combined mixture of (a) and (b) has a pH in the range of from about 1 to about 4.5, wherein (a) and (b) are in the form of intended use, and wherein the molar level of (a) is from about 0.0003 moles (per 100g of composition) to less than about 0.09 moles (per 100g of composition).

32. Use of a composition according to any of claims 1 to 13 for coloring textiles and/or fibres.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/22718

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : A61K 7/13

US CL : 8/406

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 8/400, 406, 408

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, DIALOG

search terms: hair, keratin, dye, color, oxidative, oxidant, peroxygen, peroxide, fastness, uptake, Hunter

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,500,022 A (COTTERET) 19 March 1996, see Abstract; col. 1, lines 27-31 & 51-59; col. 3, line 46-col. 4, line 6; col. 4, lines 48-63 and Examples.	1-3, 15-31
X	US 5,391,206 A (COTTERET) 21 February 1995, see Abstract; col. 1, lines 33-40; col. 4, line 59-col. 5, line 19; col. 5, lines 54-68 and Examples.	1-3, 15-31
X	US 5,279,619 A (COTTERET et al) 18 January 1994, see Abstract; col. 1, lines 20-34; col. 4, line 45-col. 5, line 9; col. 5, line 39-col. 6, line 11 and Examples.	1-3, 15-31



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

19 FEBRUARY 1998

Date of mailing of the international search report

09 MAR 1998

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/22718**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-14 and 32
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/22718

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,207,798 A (COTTERET et al) 04 May 1993, see Abstract; col. 1, lines 21-25 & 31-39; col. 5, line 44-col. 6, line 9; col. 6, lines 41-57 and Examples.	1-3, 15-31
X	US 4,885,006 A (GROLLIER et al) 12 December 1989, see col. 2, line 6-col. 3, line 4; col. 3, lines 56-64; col. 4, lines 11-15; col. 5, lines 17-57 and Examples.	1-3, 15-31
X ---- Y	US 5,316,551 A (WENKE) 31 May 1994, see col. 1, lines 44-57; col. 4, lines 60-68; col. 6, lines 43-66; col. 11, lines 1-10 and Example 1.	22 ----- 1-3, 15, 18-21, 23-29, 31
X ---- Y	US 5,100,436 A (WENKE) 31 March 1992, see col. 1, lines 41-55; col. 4, lines 57-65; col. 6, lines 40-63; col. 11, lines 1-10 and Example 1.	22 ----- 1-3, 15, 18-21, 23-29, 31